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CONTENTS

PAGE

116. Blepherin. Part I.—By D. N. Chaudhury 621

117. Rubeanic acid and its derivatives as colorimetric reagents. Part III. *NN'*-Di-β-hydroxyethyl- and *NN'*-di-*iso*amyl-rubeanic acids.—By J. Xavier and Priyadaranjan Rây 633

118. Estimation of mercuric salts by reduction with sodium formate.—By Sameer Bose 641

119. The light scattering behaviour of thorium arsenate gel-forming systems.—By K. E. Jabalpurwala and D. M. Desai 645

120. Chemical investigations on the leaves of *Gymnema sylvestre* R. Br.—By Hari Narayan Khastgir, Sudhendu Kumar Sengupta and Pasupati Sengupta ... 650

121. Chemistry of beryllium. Part III. Compounds of beryllium chloride with aminophenols, aminobenzoic acids, *p*-nitroaniline and 2:4-dinitrophenylhydrazine.—By Sarju Prasad and Kashi Prasad Srivastava 653

122. Benzylthioureas. Part II.—By J. P. Trivedi and J. J. Trivedi 657

123. Barbiturates. Part I. 5:5-Diethyl-N^1-(substituted benzyl) and N^1-(substituted phenyl) barbiturates and thiobarbiturates.—By J. P. Trivedi and J. J. Trivedi 661

124. Potentiometric studies on the composition of manganese ferrocyanide complex.—By Ram Sahai Saxena 665

125. Formation of compounds of cuprous iodide with alkali and alkaline earth metal iodides in acetone —By Sarju Prasad and Kailash Nath Upadhyaya ... 669

126. Derivation of an equation for slow coagulation of colloids on the basis of Smoluchowski's theory.—By B. N. Ghosh 671

127. Oxyfluoborates and their chemical analogy with the sulphates. Part I. Oxyfluoborates of alkali metals, alkaline earth metals and lead.—By Asimbikash Ray and Grihapati Mitra 677

128. Behaviour of chloronitrobenzenes with hydrazine and hydrazine derivatives. Part VI. Some 2-*p*-tolylnitro-1:2:3 benzotriazoles and their 1-oxides.—By Shiam Sunder Joshi and Satya Prakash Gupta 681

129. Barbiturates. Part II. 5-Methyl-5-substituted benzyl barbiturates and thiobarbiturates.—By J. P. Trivedi and J. J. Trivedi 687

130. Oxyfluoborates and their chemical analogy with the sulphates. Part II. Oxyfluoborates of Cu, Zn, Cd, Co and Ni.—By Asimbikash Ray and Grihapati Mitra 690

Short Notes:

16. The sapogenin from the seeds of *Achyranthes aspera* Linn.—By Hari Narayan Khastgir, S. K. Sengupta and P. Sengupta 693

17. *dl*-Serine.—By S. K. Guha and J. N. Ray 695

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[Jour. Indian Chem. Soc., Vol. 35, No. 9, 1958]

BLEPHERIN. PART I

By D. N. Chaudhury

The glucoside 'blepherin', obtained from the seeds of *Blepheris edulis*, Pers. (N.O. Acanthaceae), has been assigned the formula $C_{17}H_{20}O_{10}$, $2H_2O$. Based on chemical studies of the hydrolytic fission products and the I. R. and U. V. data, it is tentatively proposed that blepherin is 3:4-dihydro-5-β-D-glucosyloxy-9-hydroxy-(x)-dihydrofurano-*iso*coumarin (II or III: R = H; R_1 = glucosyl). It seems to be the first dihydrofurano-dihydro*iso*coumarin to be detected in nature.

Blepherin, a colorless crystalline bitter principle, was first isolated by Lal (this *Journ l*, 1936, **13**, 109; 1940, **17**, 269) from the seeds of *Blepheris edulis*, Pers, to which he assigned the formula $C_{16}H_{20}O_{10}$, 1.5 H_2O, m.p. 220°; $[\alpha]_D^{31\cdot5}$ + 121°.5. He reported the preparation of its penta-acetyl, pentacarbethoxy and penta-*p*-nitrobenzoyl derivatives. Although on hydrolysis with dilute hydrochloric acid he claimed to have isolated a crystalline aglycone, m.p. 178°, neither its analytical results nor the experimental details of hydrolysis were recorded. Besides, he inferred that blepherin was a β-glucoside as it had been hydrolysed by emulsin; but he made no investigation of the hydrolytic fission products nor did he undertake the characterisation of the sugar moiety.

The first approach aimed at repetition of Lal's method of isolation, followed by hydrolysis of blepherin and structural investigation of the hydrolytic fission products. As the tedious method of isolation followed by Lal gave a very poor yield, a simpler process has been developed to obtain blepherin in fairly good quantities (0.7% of the seeds); its m.p. by repeated crystallisations could be raised to 225-26°; $[\alpha]_D^{32} = +121°.3$. Contrary to the claims made by Lal (*loc. cit.*), molecular weight determinations of its derivatives by Rast's camphor method (M.W. of blepherin itself could not be determined by this method as it was insoluble in camphor) as well as the analyses of blepherin and its derivatives indicate the empirical formula of blepherin as $C_{17}H_{20}O_{10}$, $2H_2O$. The acetylation of blepherin has, however, been achieved under two different milder experimental conditions and the m.p. of the acetate in each case was found to be 158-59° (Lal records m.p. 183°). The same product was invariably obtained even when the acetylation was done under the rather drastic condition, adopted by Lal. Moreover, the analytical results of the crystalline acetate, based on the formula now assigned to blepherin, showed the presence of five hydroxyl groups.

Contrary to the claim by Lal, the author failed to isolate the aglucone by repeated attempts to hydrolyse blepherin, under varying conditions. The neutralised aqueous solution, however, readily reduced hot Fehling's solution and Tollen's reagent, indicating the presence of a reducing sugar in the solution, since blepherin itself

has no such reducing properties at all. Failure to isolate the aglucone by acid hydrolysis may be attributed to some deep-seated change in the molecule in acidic medium, although the glycosidic nature of blepherin is clearly demonstrated. Final confirmation of its β-glucosidic character came from the fact that hydrolysis of blepherin by emulsin could satisfactorily be effected, the aglucone, $C_{11}H_{10}O_5$, being slowly deposited from the solution as yellow needles on standing, and on rigorous purification it was obtained as colorless needles, m.p. 207° (Lal records m.p. 178°). From the carbohydrate remaining in the aqueous solution, phenyl-D-glucosazone was isolated and characterised, showing that only D-glucose was formed during the hydrolysis. The hydrolysis of blepherin may therefore be represented as:

$$C_{17}H_{20}O_{10} + H_2O = C_{11}H_{10}O_5 + C_6H_{12}O_6.$$

For the sake of convenience, it is proposed to name the aglucone $C_{11}H_{10}O_5$ as 'blepherigenin'.

Although blepherigenin does not give any colour reaction with ferric chloride, that it is a dihydric phenolic compound is confirmed from its following behaviours: (*a*) it readily dissolves in cold aqueous caustic alkalies from which it is reprecipitated by carbon dioxide; (*b*) it yields a diacetate and a dibenzoate by Schotten-Baumann method of acylation; (*c*) it forms a neutral dimethyl ether with alkaline dimethyl sulphate or methyl iodide-potassium carbonate, and (*d*) it rapidly reduces hot Fehling's solution and Tollen's reagent (polyhydric phenols). As blepherigenin fails to respond to the fluorescence test, it is not possibly a *meta*-dihydroxyphenolic compound with the free *para* position. On the other hand, the two phenolic groups appear to be in *ortho* or in *para* positions, as its alkaline solution rapidly undergoes oxidation in air. Thus, when pure blepherigenin, which is colorless, is dissolved in aqueous caustic soda, the solution immediately becomes yellow; on keeping at room temperature it turns deep brown and overnight it becomes dark coloured, and a humus-like material with metallic shine gradually separates. Besides, on oxidation with ferric chloride or with alkaline ferricyanide it readily gives rise to similar intractable products. Although for want of sufficient material it has not been possible so far to confirm the precise orientation of the two phenolic groups, preliminary experimental evidences, however, favour the *para* positions. Thus, failure on the part of blepherigenin to respond to the usual distinctive tests of an *ortho*-dihydroxyphenol, such as colour reaction with ferric chloride or ammonium molybdate and precipitation with basic lead acetate, is not inconsistent with the view that blepherigenin, in all probability, is a *para*-dihydroxyphenolic compound.

Examination of the infra-red spectrum of blepherigenin dimethyl ether reveals the presence of a conjugated δ-lactone. A comparison of its carbonyl stretching frequency with those of mellin methyl ether (3:4-dihydro-8-methoxy-3-methyl*iso*-coumarin; Blair and Newbold, *J. Chem. Soc.*, 1955, 2872) and of 7-methoxy-phthalide (Duncanson *et al.*, *J. Amer. Chem. Soc.*, 1953, **75**, 1331), both in solution

and in the solid state, given below, strongly suggests the existence of a dihydro-*iso*coumarin ring in blepherigenin dimethyl ether.

Blepherigenin dimethyl ether	...	1708 cm^{-1}	(solid)	...	1720 cm^{-1} ($CHCl_3$)
Mellin methyl ether	...	1710	(solid)	...	1741 (CCl_4)
7-Methoxyphthalide	...	1748	(solid)	...	1782 (CCl_4)

This conclusion is in keeping with the view that the carbonyl frequencies in the cases of lactones, lactams and cyclic ketones increase as the size of the ring diminishes (Rusmussen and Brattain, *J. Amer. Chem. Soc.*, 1949, **71**, 1073).

Furthermore, Blair and Newbold (*loc. cit.*) have observed that in the ultraviolet region the strong bathochromic shift of the maxima in dihydro*iso*coumarins, compared with those in the phthalides, is so noteworthy that it might be of diagnostic use in deciding between the isomeric dihydro*iso*coumarin and phthalide structures. Thus, when the ultraviolet absorption spectrum of blepherigenin is compared with those of mellin and the phthalides (Blair and Newbold, *loc. cit.*) the bathochromic shift of the maxima in blepherigenin is found pronounced, and therefore it strongly supports the presence of a dihydro*iso*coumarin ring.

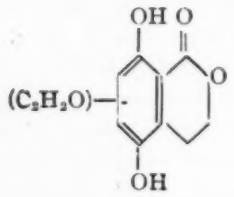
	$\lambda_{max.}$	$\varepsilon_{max.}$
Blepherigenin	2590 Å	13,437
Mellin	2460	6,500
7-Hydroxyphthalide	2320	8,700
7-Hydroxy-3-methylphthalide	2320	7,500
7-Hydroxy-3-ethylphthalide	2340	7,000

Conclusions from the chemical studies are also in conformity with the foregoing inference. Although the neutral dimethyl ether of blepherigenin is insoluble in aqueous caustic potash (40%), the presence of a lactone ring is deduced by its behaviour towards boiling alcoholic alkalies. The sodium or potassium salt of the lactone, which was eventually isolated as a solid, readily dissolved in water and the aqueous solution, on acidification, immediately deposited the original dimethyl ether. Since the lactone ring is very stable, all attempts to prepare its derivatives (e.g., hydrazide formation, methanolysis with sodium methoxide, esterification with dimethyl sulphate or dizomethane) have so far not met with success; but reduction with lithium-aluminium hydride to the corresponding diol has, however, been successfully effected, and the presence of the lactone ring thus substantiated.

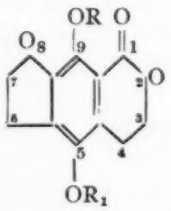
In blepherigenin ($C_{11}H_{10}O_5$), the functional groups containing all the oxygen atoms have been accounted for as follows: Out of the *five* oxygen atoms, *two* are accounted for in the phenolic hydroxyl groups; *two* in the lactone ring of the dihydro*iso*coumarin, and the remaining *one*, in the absence of any alkoxy (Zeisel) or ketonic (the dimethyl ether failed to react with Brady's reagent, hydroxylamine, semicarbazide; no characteristic absorption in the I.R.) or alcoholic group (the dimethyl ether did not react with acetic anhydride, 3:5-dinitrobenzoyl chloride; no characteristic absorption in the I.R.), presumably must be present in ether

linkage. Moreover, blepherigenin does not contain any ethylenic double bond because its dimethyl ether does not give the usual tests for unsaturation, nor can it be catalytically hydrogenated. Besides, it fails to respond also to Legal's test for βγ-unsaturated lactone. The Kühn-Roth oxidation of the aglucone with chromic acid fails to give acetic acid, and therefore absence of *C*-methyl in blepherigenin is indicated.

Some deductions may now be made as to the nature of the nuclei. Blepherigenin, as best representing the facts so far known, is a *para*-dihydroxy-dihydro*iso*coumarin compound, and therefore the partial structure (I) may be assigned to it. Since it is optically inactive, substitution at 3:4-positions is eliminated; the absence of *C*-methyl is also indicated by the negative Kühn-Roth determination. In view of the fact that one oxygen atom is present in ether linkage and that there is no unsaturation in the molecule, the moiety C_2H_2O must represent a single saturated ring, and the only possible way to accommodate this moiety is in the form of a dihydrofurano ring. This gives rise to two possibilities, and the structure of blepherigenin may thus be provisionally represented as (II) or (III).



(I)



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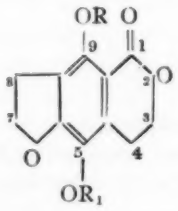

(III)

Although confirmatory evidence is at present lacking, certain experimental observations suggest the existence of the dihydrofurano ring. Traces of a phenolic acid, obtained by caustic potash fusion of blepherigenin dimethyl ether (II or III: R=R_1=Me), gave intense port-wine colour with alcoholic ferric chloride, thereby indicating the creation of a new phenolic group, presumably caused by the fission of the postulated furano ring. Moreover, zinc dust distillation of blepherigenin yielded minute quantities of a sublimate which also gave a port-wine colour with ferric chloride (blepherigenin itself does not give colour with ferric chloride)—evidently again due to a new phenolic group formed by the rupture of the furano ring. The quantities of the phenolic products, in both the cases, were too meagre to permit isolation and characterisation. However, the final choice between the structures (II) and (III) will be the subject of the next communication.

The orientation of the glucose residue in blepherin has been determined as follows. Evidence bearing on the chelated condition of *one* phenolic group in blepherigenin and, hence, its proximity to the carbonyl group of the lactone (incidentally established the presence of a *conjugated* lactone) was found in the

failure of *one* of the two phenolic hydroxyls to react with diazomethane Thus, while blepherigenin with diazomethane yielded the monomethyl ether (A) (II or III: R=H ; R_1=Me), m.p. 163°, blepherin, on prolonged methylation with MeI-K_2CO_3 and subsequent hydrolysis of the glucosyloxy group by emulsin, gave blepherigenin monomethyl ether (B), m.p. 154°. An admixture of the two *isomeric* monomethyl ethers, (A) and (B), melted at 132-42° with previous sintering at 127°. This establishes that the monomethyl ether (B) is different from its isomer (A), and must therefore have the structure (II or III: R=Me ; R_1=H). Consequently it follows that the structure of blepherin may be (II or III: R=H; R_1=glucosyl). The two monomethyl ethers, (A) and (B), on further methylation with MeI-K_2CO_3, as expected, furnished the same dimethyl ether (II or III: R=R_1=Me), obtained directly from blepherigenin by the action of methyl iodide and potassium carbonate.

During recent years, quite a number of natural products having the *iso*coumarin or dihydro*iso*coumarin structures have been reported, but the existence of a hitherto-unreported dihydrofurano-dihydro*iso*coumarin is noteworthy and creates interest. For final confirmation of the proposed structure of blepherin, further investigation, both by degradative and synthetic methods, is in progress.

EXPERIMENTAL *

Isolation of Blepherin (II or III: R=H ; R_1=glucosyl).—The seeds of *Blepheris edulis*, Pers. (5 kg., batches of 200 g.) were finely powdered and refluxed with acetone (800 c.c. for 200 g.) for 2 hours and the extract was filtered. The extraction was repeated with fresh acetone thrice altogether. The combined extract was freed of acetone as completely as possible by distillation and the residue was set aside for a weak, when a thick crystalline mass with dark oily impurities separated. It was then refluxed with ethyl acetate (250 c.c.) for 2 hours and after keeping overnight, the crystalline solid was filtered off. The dark brown crystals, thus obtained, were again boiled with ethyl acetate (100 c.c.) for 1 hour, left for 6 hours, and then filtered. The brown solid was collected and dissolved in the minimum quantity of hot water; on keeping, the aqueous solution solidified to a thick paste of needles. Three to four crystallisations from the minimum quantities of hot water removed most of the colouring matter from the crystals. Three further crystallisations from boiling alcohol, followed by two crystallisations from hot water, yielded the colorless crystals (18 g.) free from allantoin with which it was contaminated.

Concentration of the combined aqueous and alcoholic mother-liquors gave further quantities of blepherin, largely contaminated with allantoin. Allantoin was removed as follows: Impure blepherin was dissolved in the minimum quantity of boiling water and the hot solution was seeded with pure blepherin when immediately crystalline needles separated, multiplying to a thick paste. The vessel was then kept in a bath of cold water for five minutes and immediately filtered, even

* All m.p.s are uncorrected. Micro-analyses were done by Drs. Weiler & Strauss, Oxford, and by Dr. Gore, Dept. of Chemical Technology, Bombay Univ.

though the solution was warm. Two to three such operations usually purified the blepherin and made it free of allantoin (N test negative). Again the mother-liquors were worked up thus to recover blepherin (19 g.); total yield 35 g. of blepherin from 5 kg. seeds (0.7%). A very pure specimen, obtained by repeated crystallisations from ethyl alcohol had m.p. 225-26°; $[\alpha]_D^{28}$ +121°.3 (*c*, 0.03135 g. in water). (Found: C, 48.98, 48.97, 48.70; H, 5.57, 5.97, 5.60. Calc. for $C_{17}H_{20}O_{10}$, $2H_2O$: C, 48.57; H, 5.71%). [Found (in a specimen dried in a vacuum at 150° to const. wt.): C, 52.06; H, 5.38; loss of H_2O, 6.51, 6.11. Calc for $C_{17}H_{20}O_{10}$, $0.5H_2O$: C, 51.9; H, 5.34; loss of H_2O, 6.4%].

Blepherin crystallises from water in long colorless needles; on keeping for a few days in contact with water, these needles changed to beautiful rectangular plates. It is soluble in hot ethyl and methyl alcohols, insoluble in ethyl acetate, benzene, chloroform, acetone and petroleum ether. It readily dissolves in aqueous alkalies from which it is reprecipitated on acidification with mineral acids. It is difficultly soluble in cold HCl (conc.); the colorless solution on boiling becomes intense yellow. It is insoluble in cold H_2SO_4 (conc.); on warming, the solution becomes pink and finally is charred when heated. The aqueous or alcoholic solution of blepherin does not give any colour reaction with ferric chloride; it does not respond to Legal's test, nor does it reduce Fehling's solution. It has no unsaturation ($KMnO_4$ and Br_2 in CCl_4 not decolorised) and has no alkoxy group (Zeisel negative).

Blepherin Penta-acetate (II or III: R=CH_3CO; R_1=tetra-aceto-glucosyl)

(*a*). Blepherin (0.2 g.) (dried for 5 hours in vacuum at 120°), dissolved in warm pyridine (1 c.c.), was mixed with acetic anhydride (2 c.c.) and allowed to stand at the room temperature for 24 hours. The solid acetate, isolated in the usual way, was crystallised from the minimum quantity of methyl alcohol; a few further recrystallisations from dilute methyl alcohol furnished blepherin penta-acetate as colorless felted needles, m.p. 158-59° (slow heating), with previous sintering (prolonged) at 122°. [Found: C, 51.95, 52.11; H, 5.42, 5.35; M.W. (Rast), 598, 600. $C_{17}H_{15}O_{10}(CH_3CO)_5$, $1.5H_2O$ requires C, 52.17; H, 5.31%; M.W., 621].

(*b*). A mixture of dried blepherin (0.1 g.), acetic anhydride (3 c.c.), fused sodium acetate (0.5 g.) was heated for 2 hours on a water-bath and worked up in the usual way. Two crystallisations from dilute methyl alcohol yielded the *acetate* as felted needles, m.p. and mixed m.p. 158-59°, with previous sintering at 122°.

(*c*). Repetition of Lal's method (*loc. cit.*, 1940) gave the same *acetate*, m.p. and mixed m.p. 158-59°, sintering at 122°.

Blepherigenin (II or III: R=R_1=H): *Acid Hydrolysis.*—Blepherin (1.0 g.) was refluxed with dilute H_2SO_4 (50 c.c., 2%) for 5 hours, when the initially colorless solution became red; on keeping, the solution gradually became darker and no solid was deposited. Ether extract of the acid solution gave only traces of the unchanged starting material. The reaction mixture was then carefully neutralised with $BaCO_3$ and filtered; the neutral red filtrate, on keeping, deposited slowly a dark brown, humus-like solid during the course of a week, which could not be crystallised. The aqueous solution, however, readily reduced hot Fehling's solution.

The same result was obtained when the hydrolysis was carried out with methanolic aq.HCl (8%). The solution after refluxing became dark red from which a deep brown intractable material was obtained.

Hydrolysis with oxalic acid solution (5%) gave a similar dark-coloured solid which failed to crystallise.

Hydrolysis with Emulsin.—Blepherin (2 g., 10 batches), dissolved in water (75 c.c.) at room temperature, was treated with a little emulsin and allowed to stand at a warm place (30-32° preferably) with the mouths of the flasks plugged in with cotton. After 3-4 days, the initially colorless solution became yellow and traces of a yellow solid material started separating; a little emulsin was further added at this stage and set aside. During the course of a fortnight from the start of the experiment, fairly appreciable quantities of solid (in some flasks the solid had yellow colour and in some, red) were deposited from the yellow supernatant liquid and, as traces of fungus were noticed, it was worked up without further delay. The yellow/red precipitate was filtered off from the aqueous solution (P), dissolved in warm methyl alcohol and filtered from insoluble impurities; the clear methanolic solution, on concentration on a water-bath, almost solidified to a paste of tiny yellow needles. A few crystallisations from boiling water yielded blepherigenin as yellow needles, m.p. 205°. Further quantities of blepherigenin were recovered from the aqueous solution (P). Concentration on a water-bath under reduced pressure gave a thick paste of yellow/red needles of blepherigenin, contaminated with the unchanged blepherin. Repeated crystallisations from hot water (the solubility of blepherin in hot water is much greater than that of blepherigenin) finally furnished the aglucone as pale yellow needles, m.p. 205°. Working up in this way a total of 6.5 g. of blepherigenin was collected.

A specimen of blepherigenin was purified by dissolving in aqueous NaOH, precipitating it by CO_2 and then crystallising repeatedly from a mixture of dioxan-petroleum ether (b.p. 60-80°) and finally from dioxan, when colorless prismatic needles, m.p. 207°, were obtained; λ_{max} 2500Å (ε 13434), 2800Å (ε 7513); λ_{min} 2290Å (ε 6509), 2720Å (ε 6378). [Found: C, 58.4, 58.8, 58.53; H, 5.0, 4.5, 4.35; M.W (Rast) 205, 220. $C_{11}H_{10}O_5$ requires C, 59.4; H, 5.0%; M.W., 222).

Blepherigenin sublimes under vacuum at 120° to colorless needles, m.p. 207°. Purification by this method was found wasteful as charring occurred on continued heating.

Another method to obtain colorless needles was to dissolve the red/yellow needles of blepherigenin in boiling water and to add a drop of HCl (conc.), followed by a small amount of zinc dust. On quickly filtering the hot colorless solution, colorless needles separated out on cooling which were soon filtered off as otherwise, on keeping in solution the crystals became coloured again. This procedure was, however, found to be also wasteful.

The red/yellow crystals of blepherigenin, when dissolved in the minimum quantity of dilute aq.alkalies and acidified with dilute HCl, a thick paste of pale yellow needles was obtained. On repeating this process thrice, the colour gradually

became much paler, but another repetition furnished the aglucone as intensely coloured as the original specimen.

Properties of the Aglucone, Blepherigenin.—It readily dissolves in cold aqueous alkalies, imparting a yellow colour to the solution; dilute mineral acids, even CO_2, reprecipitate the original compound. The alkaline solution overnight becomes dark brownish red and after a few days a deep brown amorphous solid with metallic shine separates out. It is insoluble in cold aq.Na_2CO_3 and aq.$NaHCO_3$. Oxidation with $FeCl_3$ or alkaline ferricyanide gives a dark brown precipitate. It does not give colour with aqueous alcoholic $FeCl_3$ nor does it respond to Legal's test. It readily reduces hot Fehling's solution and Tollen's reagent. It fails to give the flourescence test or colour with ammonium molybdate. No precipitate is obtained with basic lead acetate solution. Its alkaline solution gives a brown precipitate with benzene diazonium chloride solution. Oxidation with chromic acid (Kühn-Roth) to determine the *C*-methyl failed to give acetic acid. It is not soluble in cold H_2SO_4 (conc.), but on warming it dissolves with a wine-red colour. It is insoluble in cold HCl (conc.), but on boiling it dissolves, imparting a yellow colour to the solution.

Characterisation of the Sugar Moiety.—The aqueous solution, left after the isolation of blepherigenin and unchanged blepherin in the foregoing hydrolysis experiment, was concentrated under reduced pressure to a thick syrup, taken up in a little water and filtered from the insoluble residue. A test portion of the aqueous solution immediately reduced Fehling's solution. Aqueous phenylhydrazine acetate (0.4 c.c. of a mixture containing phenylhydrazine 10 c.c., acetic acid 10 c.c., diluted to 25 c.c. with water) was added and after 5 minutes at 100°, a precipitate formed (required for the formation of D-glucosazone, 4-5 minutes). One hour later, the mixture was cooled, the osazone collected and purified by crystallisation from dilute alcohol. Its crystalline form was identical with that of a specimen similarly prepared from D-glucose and after recrystallisation from dilute alcohol it had m.p. and mixed m.p., 204-205° (with rapid heating). (Found : C, 60.6 ; H, 6.2 ; N, 15.4. Calc. for $C_{18}H_{22}O_4N_4$: C, 60.3 ; H, 6.4; N, 15.6%).

Blepherigenin Diacetate (II or III : $R=R_1=CH_3CO$).—A solution of blepherigenin (0.2 g.) in NaOH (5 c.c., 2*N*) was mixed with acetic anhydride (5 drops) and a little crushed ice. On vigorous shaking, immediately a solid separated out which on recrystallisations from dilute methyl alcohol yielded the pure *diacetate*, m.p. 177°, with previous sintering at 173°. [Found : C, 57.4 ; H, 4.4. $C_{11}H_8O_3(CH_3CO)_2$, $0.5H_2O$ requires C, 57.2; H, 4.9%]. [Found in a specimen dried in vacuum at 110° : C, 58.3; H, 4.6. $C_{11}H_8O_6(CH_3CO)_2$ requires C, 58.8 ; H, 4.9%].

A solution of blepherigenin in pyridine was treated with acetic anhydride, allowed to stand for 24 hours and worked up in the usual way, when the *acetate* was obtained, m.p. and mixed m.p. 177°.

Blepherigenin Dibenzoate (II or III : $R=R_1=PhCO$).—Blepherigenin (0.2 g.), dissolved in NaOH (10 c.c., 2*N*), was treated with benzoyl chloride (4 drops) and shaken until a solid separated out. Several recrystallisations from methyl alcohol gave colorless needles, which on further crystallisation from ethyl acetate furnished

the *dibenzoate* in rectangular prisms, m.p. 207°. [Found: C, 66.6, 67.04; H, 4.05, 4.14. $C_{11}H_8O_3(C_6H_5CO)_2,H_2O$ requires C, 66.9; H, 4.4%]. [Found in a specimen dried over P_2O_5 in a vacuum desiccator: C, 68.3; H, 4.5 $C_{11}H_8O_3(C_6H_5CO)_2,0.5H_2O$ requires C, 68.3; H, 4.3%].

Blepherigenin Dimethyl Ether (II or III: $R=R_1=CH_3$).—To ensure success it is essential that blepherigenin should be as little coloured as possible, otherwise the yield of the dimethyl ether is considerably lowered. Different samples (red and yellow) of blepherigenin (10 g.) were taken together and dissolved in the minimum quantity of cold NaOH solution (2*N*) when a dark solution was obtained. A current of CO_2, washed through water, was passed until the solution became saturated and the phenolic compound completely separated out. The crystals of blepherigenin were again similarly treated and finally crystallised from boiling water (charcoal), when very pure pale yellow needles (9.55 g.), m.p. 207°, were obtained. These were thoroughly dried in an oven at 110°,

(*a*). The purified dry blepherigenin (3 g.), dissolved in anyhdrous pure acetone (100 c.c.), was refluxed with methyl iodide (10 c.c.) and anhydrous K_2CO_3 (8 g.) for 10 hours. The inorganic salts were filtered off from the solution and washed with portions of warm acetone. The filtered solution was then evaporated, and the residue washed with dilute NaOH, followed by water, and dried in a desiccator (3.5 g. of the dimethyl ether obtained from 9 g. of blepherigenin). Vacuum distillation (1 mm/bath temp., 180-85°) of the methyl ether gave colorless distillate which soon solidified to colorless needles. One crystallisation from dilute methyl alcohol (ice-chest) yielded the pure *blepherigenin dimethyl ether* as silky needles, m.p. 71° (5 g. from 5.5 g. of the crude dimethyl ether). [Found: C, 62.2, 62.3; H, 5.8, 6.0; OMe, 24.8; M.W. (Rast), 235. $C_{11}H_8O_3(OMe)_2$ requires C, 62.4; H, 5.6; OMe, 24.8%; M.W., 250].

Unlike blepherigenin, it does not reduce Fehling's solution or Tollen's reagent; it is insoluble in aq. alkalies. It does not decolorise aq. $KMnO_4$, Br_2 in CCl_4 and does not absorb hydrogen on Pd-C catalyst in methyl alcohol at room temperature. On refluxing with Ac_2O-NaAc the unchanged material is obtained. It does not form 2:4-dinitrophenylhydrazone, oxime and 3:5-dinitrobenzoate. It fails to give colour test with gallic acid and H_2SO_4 (conc.) for methylenedioxy group. With H_2SO_4(conc.) in cold it gives no colour, but on warming a violet colour is produced. It is insoluble in cold HCl (conc.) and unlike blepherigenin, on boiling it neither dissolves nor imparts any colour.

(*b*). To a solution of blepherigenin (0.5 g.) in aq. NaOH (5 c.c., 2*N*) dimethyl sulphate (4 c.c.) was added in portions alternated with aq.NaOH (25 c.c., 2*N*) to keep the solution alkaline all the time. It was warmed occasionally to maintain the temperature at 40-60° and the mixture shaken during the operation. After 3 hours a dark oil separated which was extracted with ether, and the extract washed with water. The ethereal solution after drying over Na_2SO_4, on evaporation, left a red oily residue which on keeping or on seeding deposited the *blepherigenin dimethyl ether* in clusters of prismatic needles. A few crystallisations from dilute methyl

alcohol (ice-chest) afforded the pure methylated product, m.p. and mixed m.p. 70°. The yield by this method was much lower than the MeI-K_2CO_3 method.

Blepherigenin Monomethyl Ether (A) (II or III: R=H; R_1=CH_3).—Blepherigenin (1 g.), dissolved in methyl alcohol (30 c.c.), was treated with an ethereal solution of diazomethane (from 5 g. of nitrosomethylurea) and left overnight. The brownish solution next day was refluxed until the colour changed to pale yellow; the ether was evaporated off and the residual liquid taken up in a little methyl alcohol and water was added to turbidity. After keeping it in the refrigerator for 2 days crystalline needles separated. Repeated crystallisations from dilute methyl alcohol (refrigerator) furnished the pure *monomethyl ether* as colorless needles, m.p. 163° (Found: C, 60.6; H, 4.8; OMe, 13.4. $C_{11}H_9O_4$.OMe requires C, 61.0; H, 5.0; OMe, 13.1%).

It dissolves in aq. NaOH and is reprecipitated on acidification. On further methylation with MeI-K_2CO_3 it yields the dimethyl ether, m.p. and mixed m.p. 71°.

Blepherigenin Monomethyl Ether (B) (II or III: R=CH_3; R_1=H).—A mixture of blepherin (2 g.), anhydrous K_2CO_3 (7 g.), MeI (7 c.c.) and pure anhydrous acetone (150 c.c.) was refluxed for 24 hours. After filtration and evaporating off the acetone, a colorless viscous oil was left which could not be crystallised. It was taken up in a little cold water in which it was soluble; the aqueous solution was treated with emulsin and set aside. After a fortnight, colorless rosettes of needles separated which were dissolved in the minimum quantity of hot methyl alcohol, water added to turbidity and left in the refrigerator; beautiful colorless needles were gradually deposited which on two crystallisations from dilute methyl alcohol (refrigerator) gave the *monomethyl ether* (B) in slender needles, m.p. 154°. [Found: C, 60.4; H, 5.3. $C_{11}H_9O_4$.OMe requires C, 61.0; H, 5.0%). When mixed with the monomethyl ether (A), it melted at 130-42°, with previous sintering at 127°.

On further methylation with MeI-K_2CO_3 it yielded the dimethyl ether, m.p. and mixed m.p. 71°.

Characterisation of the Lactone Ring

(*a*). Blepherigenin dimethyl ether (0.2 g.), dissolved in alcoholic KOH (10 c.c., 40%), was refluxed for 2 hours and the solution after dilution with a little water was concentrated on a water-bath to a very small bulk (*ca.* 2-3 c.c.). The oily potassium salt separating on ice-cooling solidified. It was dissolved in water and acidified with HCl (dil.), when the original starting material was precipitated. When the solution of potassium salt was cooled to 0° and acidified with minimum ice-cold acetic acid, the original dimethyl ether was obtained instead of the free acid.

(*b*). *Lithium-Aluminium Hydride Reduction of the Lactone Ring.*—To an ice-cold suspension of $LiAlH_4$ (1.0 g.) in anhydrous ether (60 c.c.) blepherigenin dimethyl ether (1.0 g.) was added in portions and the mixture shaken for 2 hours at room temperature. It was then again cooled in ice, treated with water (not much excess) and left in the refrigerator overnight. The ether layer was decanted and

the residue extracted with fresh portions of ether; the combined ethereal solution was washed repeatedly with water till the washings were neutral to litmus. Evaporation of the ether after drying with $MgSO_4$ gave a syrupy residue, which when rubbed with a littte petrol-ether (b.p. 40-60°), afforded crystals contaminated with brown oily impurities. After decanting the petrol-ether it was repeatedly triturated with petrol-ether (or preferably with CCl_4) to remove the oily impurities and the almost colorless crystals, thus obtained, were dissolved in the minimum quantity of petrol-ether (40-60°); on standing in the refrigerator the *diol* crystallised out in colorless rosettes of needles. A few such crystallisations furnished the pure product, m.p. 84°. (Found: C, 61.8, 61.6; H, 6.2, 6.5. $C_{13}H_{18}O_5$ requires C, 61.4; H, 7.0%).

(*c*). *Lactone Ring – opening Experiments.*—(*i*). *Attempted Methanolysis.*—Blepherigenin dimethyl ether (50 mg.), dissolved in methyl alcohol (5 c.c.), was treated with NaOMe solution (2 drops, 1.0 g. Na in 25 c.c. MeOH) and left for 24 hours. On acidification with acetic acid, evaporating off of the MeOH and addition of water, the unchanged starting material separated out.

(*ii*). *Attempted Hydrazide Formation.*—Blepherigenin dimethyl ether (50 mg.), hydrazine hydrate (2 drops) and alcohol (10 c.c.) were refluxed for 6 hours and on working up, the unchanged material was obtained.

(*iii*). *Attempted Esterification with* Me_2SO_4.—Blepherigenin dimethyl ether (0.5 g.), dimethyl sulphate (1.5 c.c.), K_2CO_3 (3 g.) and pure anhydrous acetone (50 c.c.) were refluxed for 100 hours. On working up in the usual way, yellow oily residue was left which on vacuum-distillation yielded the unchanged starting material.

Alkali Fusion of Blepherigenin Dimethyl Ether.—Blepherigenin dimethyl ether (0.5 g.) was fused with KOH (2.5 g.) in a nickel crucible at 250° for an hour. The cooled product was digested with water and the brown aqueous solution, after acidification with HCl, was extracted with ether. The extract was washed with 10% aq. $NaHCO_3$ and water, dried and on evaporation of the ether, traces of a sticky yellow product were obtained which could not be crystallised.

The bicarbonate washings were acidified with HCl, and extracted with ether; the yellow ethereal solution on evaporation afforded a brown gummy residue which could not be induced to crystallise. It was readily soluble in bicarbonate with effervescence and with alcoholic ferric chloride gave a port-wine colour. The product, presumably a phenolic acid, was too meagre to permit purification and characterisation.

Zinc dust Distillation of Blepherigenin.—An intimate mixture of blepherigenin (0.5 g.) and Zn dust (8 g.) was heated in a pyrex test tube with a cold fingure at 220°; pale yellow needles which sublimed in the beginning, gradually turned to reddish oily liquid. The oily sublimate, when dissolved in petroleum ether and evaporated, deposited almost colorless needles which were insufficient for purification and identification. The sublimate in alcoholic solution gave a port-wine colour with ferric chloride and rapidly became oxidised to a dark brown amorphous material in dilute alkali.

Blepherigenin dimithyl ether, when subjected to the zinc dust distillation, sublimed off unchanged at 160-70°.

Alkaline Permanganate Oxidation.—Blepherigenin dimethyl ether (1.0 g.), suspended in water (30 c.c.) containing NaOH (2 g.), was kept boiling while aqueous permanganate (4 %) was added dropwise with stirring to a 10 minutes' end-point (*ca.* 228 c.c. of the $KMnO_4$ solution required). When worked up in the usual way, a bicarbonate-soluble acidic material was obtained. The quantity being too small, it could not be purified for characterisation.

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RUBEANIC ACID AND ITS DERIVATIVES AS COLORIMETRIC REAGENTS. PART III. *NN'*-DI-β-HYDROXYETHYL- AND *NN'*-DI-*iso*AMYL-RUBEANIC ACIDS

By J. Xavier and Priyadaranjan Rây

The effect of substitution in rubeanic acid on its reactivity as a reagent has further been investigated by examining the behaviour of (I) *NN'*-di-β-hydroxyethyl- and (II) *NN'*-di-*iso*amyl-rubeanic acids. Substitution of a hydrogen atom by a hydroxyl in the ethyl radical of diethylrubeanic acid increases the solubility of the product and of its metallic complexes (e.g. of copper) in certain solvents. Di-*iso*amyl-rubeanic acid behaves like other disubstituted alkyl derivatives. Both the reagents, if used in caustic alkali solution, retard the colour development, as in the case of the diethyl derivative (cf. Part II, this *Journal*, 1958, **35**, 589). This retardation effect is more pronounced with the increase in the chain length of the substituent. Methods for the spectrophotometric determination of copper (using I), cobalt (using II), nickel (using II), palladium (using I & II) and ruthenium (using I) have been described.

In continuation of our previous work (Parts I & II, this *Journal*, 1958, **35**, 432, 589) *NN'*-di-β-hydroxyethyl- and *NN'*-di-*iso*amylrubeanic acids have been studied as colorimetric reagents. The substitution of a hydroxyl group in the ethyl radical has been found to increase the solubility of the product and of its metallic complexes in certain organic solvents. The spectrophotometric determination of copper also has therefore been possible, using *NN'*-di-β-hydroxyethylrubeanic acid. *NN'*-Di-*iso*amylrubeanic acid behaved like other disubstituted alkyl derivatives of the acid (*loc. cit.*). Methods for the spectrophotometric determination of cobalt and nickel with this reagent have been developed in alcoholic pyridine medium as in the case of the parent compound. The use of a caustic alkali solution of the reagent was, however, found to retard the colour development. Similar retardation was observed, though to a much less extent, with *NN'*-diethyl and *NN'*-di-β-hydroxyethyl derivatives. It may be noted that as the chain length of the substituent increases, this retardation effect becomes increasingly pronounced. Curiously, however, if the alkali be added after the addition of the reagent, the formation of the coloured complex occurs as usual in all these cases. An explanation of this behaviour may, probably, be found in the structural change of the reagent in alkali solution which might hinder the assumption of a favourable configuration for the complex formation.

Experimental

Preparation of the Reagents.—The preparation and properties of *NN'*-di-β-hydroxyethylrubeanic acid, ($HO.H_2C.CH_2.NH.CS.CS.NH.CH_2.OH$), have not been reported in the literature. It was prepared, like other alkyl-substituted rubeanic acids, by warming (40-50°) rubeanic acid with an alcoholic solution of ethanolamine (in molar proportions). The product was cooled in ice, when orange-red crystals separated out along with some sulphur. These were filtered and the hydroxy compound was purified by repeated crystallisation from ethyl alcohol ; yield about 50-60% of the theoretical. (Found : N, 13.48 ; S, 31.13. Calc. N, 13.45 ; S, 30.78%).

The product forms rhombic plates from alcohol, m.p. 93-94°. It is sparingly soluble in cold water, but more easily in ethyl alcohol and other common organic solvents.

NN'-Di-*iso*amylrubeanic acid, $(CH_3)_2.CH.CH_2.CH_2.NH.CS.CS.NH.CH_2.CH_2.CH.(CH_3)_2$, was prepared by warming rubeanic acid with an alcoholic solution of *iso*amylamine (Wallach and Reinhardt, *Annalen*, 1891, **262**, 354). The substance crystallises out in yellowish plates (lit. red prisms) from alcohol, m.p. 59-60°.

Reaction with Metal Ions.—The complex compounds formed by *NN'*-di-β hydroxyethyl- and *NN'*-di-*iso*amyl-rubeanic acids with metallic salts resemble those formed by rubeanic acid and its other derivatives. The properties of these complexes are recorded in Table I.

TABLE I

Metal.	*NN'*-Di-β-hydroxyethylrubeanic acid.	*NN'*-Di-*iso*amylrubeanic acid.
Cu^{II}.	Green ppt., acquires a violet tinge on keeping (from ammonical, neutral or weakly acetic acid soln.); very sparingly soluble in benzene or toluene, but fairly soluble in pyridine (greenish yellow soln. extractable by *iso*amyl or *iso*butyl alcohol).	Green ppt. with blue tinge (from ammoniacal, neutral or weakly acetic acid soln.); very sparingly soluble in common organic solvents, but more easily in pyridine (greenish yellow colour).
Co^{II}.	Brownish yellow ppt. (from ammoniacal solution); very sparingly soluble in toluene or *iso*amyl alcohol, but fairly soluble in pyridine (orange-yellow colour, partially extractable by *iso*amyl or *iso*butyl alcohol, ethyl or amyl acetate).	Dark brown ppt. (from ammoniacal soln.); fairly soluble in benzene, toluene, chloroform, carbon tetrachloride, *iso*amyl or *iso*butyl alcohol, ethyl or amyl acetate and pyridine (orange-yellow colour, extractable by the above solvents).
Ni^{II}.	Deep violet ppt. (from ammoniacal soln.); fairly soluble in pyridine (orange-red colour, extractable by *iso*amyl or *iso*butyl alcohol, ethyl or amyl acetate).	Same as I; pyridine soln. (rose-red colour, extractable by *iso*amyl or *iso*butyl alcohol and ethyl or amyl acetate).
Pd^{II}.	Orange-red ppt. which appears on keeping the soln. (acid soln.); fairly soluble in alcohol, acetone, *iso*amyl or *iso*butyl alcohol and easily in pyridine (deep yellow colour, extractable by *iso*amyl or *iso*butyl alcohol, ethyl or amyl acetate and chloroform).	Deep red ppt. (from acid soln.); soluble in almost all the common solvents. The pyridine soln. (yellow or orange-yellow, extractable by *iso*amyl or *iso*butyl alcohol).
Ag^{I}.	Pale yellow ppt. (from neutral soln.); soluble in excess of alcohol, giving an orange-yellow soln.	Yellow ppt. from neutral soln., slightly soluble in alcohol.
Pb^{II}.	Yellow ppt. from alkaline soln., soluble in excess of alkali.	Same as I.
Pt^{IV}.	Orange-yellow soln. from which a brown ppt. separates on standing (from acid soln.).	Yellow ppt. from acid soln.
Au^{III}.	Same as above.	Golden yellow colour.
Hg^{II}.	White ppt. from neutral soln., stable towards dilute alkali.	Same as I.
Ru^{III}.	Blue colour in alcoholic acid soln.	Blue soln. from which a precipitate appears in a short time.

Spot Tests.—Copper, cobalt, nickel and palladium can be detected by the spot plate technique, under conditions similar to those stated in the case of other substituted rubeanic acids (*loc. cit.*). Copper gives a greenish black precipitate on the surface of the drops, cobalt and palladium, a yellowish brown coloration, and nickel, a pink coloration, in about five minutes after the drops are placed in the depression of the spot plate. The identification and concentration limits are shown in Table II.

TABLE II

Metal.	Identification and concentration limits.	
	NN'-Di-β-hydroxyethylrubeanic acid.	*NN'*-Di-*iso*amylrubeanic acid.
Copper	0.050γ (1 :8 × 10^5)	0.05γ (1 :8 × 10^5)
Cobalt	0.025 (1 :1.6 × 10^6)	0.03 (1 :1.3 × 10^6)
Nickel	0.025 (1 :1.6 × 10^6)	0.02 (1 :2 × 10^6)
Palladium	0.060 (1 :5 × 10^5)	0.10 (1 :3 × 10^5)

Spectrophotometric Determinations

NN'-Di-β-hydroxyethylrubeanic acid serves as a useful reagent for the determination of copper, palladium and ruthenium, but not for that of cobalt and nickel. The cobalt complex is fairly soluble in pyridine, but the resulting solution is rather unstable, especially at high concentrations of cobalt. The colour intensity of an alcoholic pyridine solution of nickel-di-β-hydroxyethylrubeanic acid was found to attain its maximum value only after a long time (about 18 to 24 hours), from preparing the solutions. The determination of nickel, using the reagent, was therefore quite unsatisfactory. Cobalt, nickel and palladium can all be determined by using *NN'*-di-*iso*amylrubeanic acid. As with *NN'*-dimethyl- and *NN'*-diethyl-rubeanic acids (*loc. cit.*), the pyridine solution of copper-di-*iso*amylrubeanic acid was found to be unstable.

Copper was, however, determined by *NN'*-di-β-hydroxyethylrubeanic acid in acetone-pyridine medium. Cobalt and nickel were estimated in alcoholic pyridine solution using *NN'*-di-*iso*amylrubeanic acid. Palladium was determined by both the reagents in alcoholic solution. Ruthenium was determined using *NN'*-di-β-hydroxyethylrubeanic acid in a manner similar to that followed for rubeanic acid (Part I, *loc. cit.*).

An alcoholic solution of the reagents (0.1%) was used in all the experiments. Unicam SP 600 spectrophotometer, glass cells of 5, 10 and 20 mm cross section and a Cambridge Bench Type p_H-meter, with glass or alkali electrodes and a saturated calomel electrode as the reference electrode, were used.

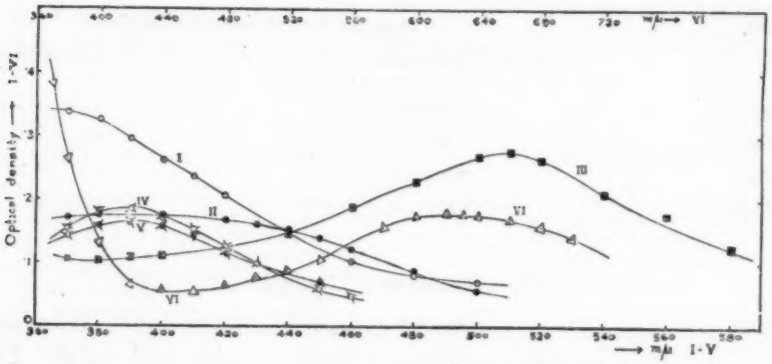
Determination of Copper

The green copper complex of *NN'*-di-β-hydroxyethylrubeanic acid dissolves in pyridine, yielding a greenish yellow solution. This affords a ready means of determining

copper spectrophotometrically. An acetone-pyridine medium was found to be the most suitable for the purpose. An alcoholic or aqueous pyridine medium, on the other hand, gives uncertain results with gradual precipitation of the complex.

FIG. 1

Absorption curves.
Cell length = 10 mm.



Curve I. Copper–di-β-hydroxyethylrubeanic acid; 2 p.p.m. Cu; p_H 10.7.
Curve II. Cobalt–di-*iso*amylrubeanic acid; 1 p.p.m. Co; p_H 10.5.
Curve III. Nickel–di-*iso*amylrubeanic acid; 2 p.p.m. Ni; p_H above 10.2.
Curve IV. Palladium–di-β-hydroxyethylrubeanic acid; 2 p.p.m Pd; p_H 3.5.
Curve V. Palladium–di-*iso*amylrubeanic acid; 1.75 p.p.m. Pd; p_H 3.5.
Curve VI. Ruthenium–di-β-hydroxyethylrubeanic acid; 2 p p.m. Ru.

Absorption maximum.—No maximum in the visible region of the spectra was observed (cf. curve I, Fig. 1). Measurements were made at 390 mμ, where the reagent blank gave comparatively a low absorption.

Pyridine concentration: 10 c.c. in 25 c.c. final volume made up with acetone. With 5 c.c. of pyridine and 1 c.c. of the reagent solution (0.1%), the test solution, containing 2 p.p.m. Cu, remained clear only for about 20 to 30 minutes, whereas when 10 c.c. of pyridine was added, the optical density of the solution remained unaltered for about 20 hours.

Reagent concentration: 1 c.c. of 0.1% alcoholic solution of the reagent was sufficient to develop the maximum intensity for copper up to 4 p.p.m.

Optimum p_H range: 10.1–11.0.

Beer's law was obeyed (cf. curve I, Fig. 2).

Stability of the colour.—The maximum intensity was reached within 5 to 10 minutes after the addition of the reagent and making up the volume with adjustment of p_H. The intensity thereafter remained unchanged for several hours at room temperature.

Sensitivity: 0.007γ Cu/cm² (Sandell) and 0.03γ Cu/cm² (practical).

Effect of diverse ions.—Many metals were found to interfere. The use of complexing agents like the disodium salt of ethylenediaminetetra-acetic acid to mask the interference due to cobalt, nickel, iron, chromium, etc., was not possible, as the copper colour due to *NN'*-di-β-hydroxyethylrubeanic acid was also partially masked.

Procedure.—To the copper solution, free from interfering ions, pyridine (10 c.c.), the reagent solution (0.1%, 1 c.c.) and acetone (10 c.c.) were added. The volume was made up to 25 c.c. with acetone, after adjusting the p_H to 10.1 to 11.0. The optical density was measured at 390 mμ against the reagent blank.

Determination of Cobalt

The orange-yellow colour of the cobalt salt of *NN'*-di-*iso*amylrubeanic acid was developed in alcoholic pyridine solution.

Absorption maximum: 380–400 mμ (cf. curve II, Fig. 1). Measurements were made at 400 mμ.

Pyridine concentration: 5 c.c. of pyridine in a total volume of 25 c.c. made up with alcohol.

Reagent concentration: 1 c.c. of 0.1% alcoholic solution.

Optimum p_H range: Above 10.2. The intensity remained unchanged above this p_H, unless the solution was made excessively alkaline.

Beer's law was obeyed up to 2 p.p.m. Co. The solutions became turbid with higher concentrations of the metal.

Stability of the colour.—A solution containing 1 p.p.m. Co (p_H 10.5) showed constant optical density for 3–5 hours. The stability of the solution decreased appreciably (precipitation occurs within 5–10 minutes) when the cobalt concentration was greater than 2 p.p.m.

Sensitivity: 0.0056γ Co/cm² (S) and 0.03γ Co/cm² (p).

Effect of diverse ions: As under rubeanic acid (*loc. cit.*).

Procedure.—To the test solution 5 c.c. of pyridine and 1 c.c. of the reagent solution were added. The p_H was adjusted to about 10.5 and the volume made up to 25 c.c. with alcohol (95%). The optical density was measured at 400 mμ against the reagent blank.

Determination of Nickel

Nickel develops a rose-red colour in alcoholic pyridine solution by the addition of *NN'*-di-*iso*amylrubeanic acid.

Absorption maximum: 510 mμ (cf. curve III, Fig. 1). The reagent solution has practically little absorption at this wave-length.

Pyridine concentration: 5 c.c. of pyridine in a total volume of 25 c.c. made up with alcohol.

Reagent concentration: 1 c.c. of the reagent solution (0.1%) in alcohol was sufficient for 4 p p.m. Ni, above which 2 c.c. of the reagent was required for the maximum development of colour.

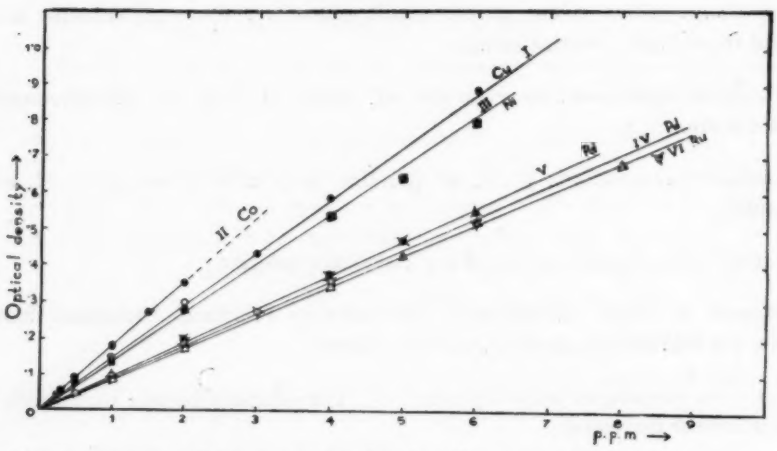
Optimum p_H range: Above 10.2; slight variations in the alkalinity of the solution above this p_H value (up to 11.5) did not affect the colour intensity.

Beer's law was obeyed (cf. curve III, Fig. 2).

FIG. 2

Beer's law curves.

Cell length = 10 mm.



Curve I. Copper - di-β-hydroxyethylrubeanic acid; 390 mμ; p_H 10.5–11.0.
Curve II. Cobalt - di-*iso*amylrubeanic acid; 400 mμ; p_H 10.2.
Curve III. Nickel - di-*iso*amylrubeanic acid; 510 mμ; p_H above 10.2.
Curve IV. Palladium - di-β hydroxyethylrubeanic acid; 390 mμ; p_H 3–4.
Curve V. Palladium - di-*iso*amylrubeanic acid; 395 mμ; p_H 3–5.
Curve VI. Ruthenium - di-β hydroxyethylrubeanic acid; 625 mμ.

Stability of the colour.—The optical density of a solution containing 6 p.p.m. Ni remained unchanged for more than 24 hours at the room temperature.

Sensitivity: 0.0073γ Ni/cm² (S) and 0.03γ Ni/cm² (p).

Effect of diverse ions: As under rubeanic acid.

Procedure.—Same as that followed for cobalt using the same reagent. After making up the volume, the optical density was measured at 510 mμ against the reagent blank.

Determination of Palladium

(*a*). *Using* NN'-Di-β-*hydroxyethylrubeanic Acid*.—When an alcoholic solution of *NN'*-di-β-hydroxyethylrubeanic acid is added to a palladium solution, an orange-yellow colour is developed.

Absorption maximum: 390 mμ (cf. curve IV, Fig. 1).

Concentration of alcohol: It was observed that a minimum concentration of about 75% ethyl alcohol in the medium was necessary to prevent the precipitation of the complex.

Reagent concentration: 1 c.c. of 0.1% alcoholic solution of the reagent was needed to develop the maximum colour intensity for palladium up to 8 p.p.m.

Optimum p_H *range*.—The colour development was almost instantaneous in slightly acid medium ($p_H \sim 1.0$); a further increase in p_H (up to 9.0) was found to have no effect on the colour intensity.

Beer's law: Obeyed up to 6 p.p.m. Pd (cf. curve IV, Fig. 2).

Stability of the colour: The optical density remained unaltered for about 24 hours.

Sensitivity: 0.011γ Pd/cm² (S) and 0.05γ Pd/cm² (p).

Effect of diverse ions.—At p_H 3–4, presence of cobalt (100γ) and nickel (10γ) can be tolerated for 2γ Pd/c.c. Lead, cadmium, zinc, manganese, etc. do not cause any interference. Addition of phosphoric acid eliminated the interference due to traces of iron (50γ for 2γ Pd/c c.), in which case the solutions were made up with 1:1 aqueous alcohol. Copper, vanadate, molybdate and tungstate, when present even in very small amounts, interfere.

Procedure.—The reagent solution (1 c.c.) was added to the palladium solution and the volume made up to 25 c.c. with ethyl alcohol after adjusting the p_H between 3 and 4. The optical density was measured at 390 mμ against the reagent blank.

(*b*). *Using* NN' *di*-iso*amylrubeanic Acid*.—The same procedure was followed as with *NN'*-di-β-hydroxyethylrubeanic acid.

Colour: Orange-yellow.

Absorption maximum: 385-395 mμ (cf. curve V, Fig. 1). Measurements were made at 395 mμ.

Alcohol and reagent concentration: Same as in the previous case.

Optimum p_H *range*: 2.5–9.0. Measurements were made at p_H 3–5.

Beer's law was obeyed up to 6 p.p.m. Pd (cf. curve V, Fig. 2).

Stability of the colour: Same as in (*a*).

Sensitivity: 0.0106γ Pd/cm² (S) and 0.04γ Pd/cm² (p).

Effect of diverse ions: Same as in (*a*).

Procedure: Same as under (*a*). The optical density was measured at 395 mμ.

Determination of Ruthenium

NN'-Di-β-hydroxyethylrubeanic acid reacts exactly in the same manner with ruthenium^{III} salt solutions as rubeanic acid itself. The same procedure (cf. Part I, *loc. cit.*) was therefore followed for the colour development. The absorption maximum was, however, found to lie between 600 and 650 mμ (cf. curve VI, Fig. 1). The minimum amount of the mixture (1 : 1) of concentrated hydrochloric acid (11 *N*) and ethyl alcohol (95%) required for the maximum colour development was 4 c.c., and the corresponding reagent concentration for Ru up to 5 p.p.m. was 1 c.c. (0.2% acetic acid solution). The optical density was measured at 625 mμ. The system obeyed Beer's law (cf. curve VI, Fig. 2) up to 8 p.p.m. Sensitivity was 0.011γ Ru/cm^2 (S) and 0.04γ Ru/cm^2 (p), *i.e.* same as for rubeanic acid.

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ESTIMATION OF MERCURIC SALTS BY REDUCTION WITH SODIUM FORMATE

By Sameer Bose

A procedure is described for evaluating mercuric salts by reducing them to metallic mercury with a 40% solution of sodium formate. The precision is 1% or better. The method with a slight modification has been used for volumetric estimation by thiocyanate solution. Neutral or acidic solutions of various salts of mercury have been successfully analysed, except for mercuric cyanide which failed to be reduced. Analysis has also been carried out in presence of other metals, mainly silver and lead, which do not interfere.

Fuchs (*Z. anal. Chem.*, 1929, **78**, 125) determined neutral alkali formates by titration of the hydrochloric acid liberated during oxidation with mercuric chloride :

$$HCOONa + 2HgCl_2 \longrightarrow NaCl + Hg_2Cl_2 + HCl + CO_2.$$

Fuchs titrated with alkali to the appearance of a yellow precipitate of mercuric oxide, but Oldeman (*Pharm. Weekblad*, 1931, **68**, 379) made the procedure more precise by titrating the acid to phenolphthalein end-point, after tying up the excess mercuric chloride with sodium chloride. Present worker has further modified this procedure (this *Journal*, 1058, **35**, 320) for microestimation of formate solutions containing one mg. of formic acid with a precision of 1%. All these facts reveal that this oxidation reaction is highly reproducible. Hence, it was felt that a reversal of this process could be used for the estimation of mercuric chloride as well. The present paper describes the determination of mercuric salts by reduction with sodium formate solution. It was noticed that on heating mercuric salts with a large excess of sodium formate for a long time, the reduction was not carried to the mercurous state only, but to metallic mercury.

Experimental

Mercuric chloride solutions were prepared by weighing chemically pure variety of the salt and dissolving it in water. Mercuric nitrate solution was obtained by dissolving pure mercury in concentrated nitric acid and diluting the solution with water after boiling off the oxides of nitrogen. Mercuric acetate solution was prepared by dissolving the salt in water and standardising it with ammonium thiocyanate solution (Scott, "Standard Methods of Chemical Analysis", 1952, p. 581) after acidifying with nitric acid. Mercuric perchlorate solution was obtained by dissolving mercuric carbonate in excess of perchloric acid and standardising it with thiocyanate solution.

Evaluation of Mercuric Chloride Solution.—A neutral solution of mercuric chloride (5-20 c.c.) containing 0.2-0.5 g. of mercury was pipetted into a 150 c.c. pyrex conical flask and treated with a 25% sodium acetate solution (5 c.c.). The acetate solution was added to suppress the H^+-ion concentration which tended to increase

during the course of the reaction and impeded its velocity. The air in the flask was driven out as far as possible by passing steam into it. The steam was only allowed to play over the solution. After quickly adding about 20 c.c. of a 40% sodium formate solution, the flask was closed with a rubber cork and heated by immersing its lower portion, containing the reaction mixture, in boiling water. Heating was continued for 3 to 5 hours till a perfect grey precipitate, frequently accompanied by small globules of mercury, was obtained. The white precipitate of calomel was sometimes found to stick to the walls of the flask and consequently it escaped the reducing action of the formate solution. In such cases, the flask was cooled, shaken well to incorporate the precipitate into the reaction mixture and then reheated. On completion of the reaction, which was indicated by the perfect grey colour of the precipitate and considerable diminution in its size, the flask was cooled and its contents filtered through a G_4 sintered glass crucible. The heavy precipitate of mercury was transferred with the help of a jet of water from a collapsible plastic wash-bottle and washed thoroughly with water. The final washing was done with 20 c.c. of acetone followed by 10 c.c. of ether. The crucible was dried in the open for about an hour and then weighed. The amount of mercury, thus obtained from the assay of six different solutions of mercuric chloride, are recorded in Table I. The error (0.2-0.6%) being always on the lower side was probably due to slight volatilisation of mercury.

TABLE I

Heated for (hrs.)	...	3	3½	4	4	5	5
Hg Found (mg.)	...	183.5	200.8	367.4	400.2	421.8	449.0
Hg Calc. (mg.)	...	184.6	201.2	369.2	402.0	423.2	450.6

Evaluation of other Salts of Mercury

(*i*). *Mercuric nitrate.*—A solution of the salt (2-5 c.c.) in dilute nitric acid was pipetted into a 150 c.c. pyrex conical flask. A 10% solution of potassium chloride (~5 c.c.) and a 15% sodium acetate solution (10 c.c.) were added, when a slight white precipitate was obtained. This precipitate did not interefere with the present procedure. After replacing the air in the flask by steam, a 40% solution of sodium formate (20 c.c.) was added in the manner already described. The reaction was completed by heating the stoppered flask for 4 to 5 hours in boiling water and the mercury obtained was washed and weighed.

(*ii*). *Solutions containing acetate, perchlorate, phosphate and iodide* (as K_2HgI_4) *of mercury* were all estimated by the above procedure and the results obtained are recorded in Table II. Neutral mercuric cyanide solutions, even on heating for a very long period with formate solution, failed to give any precipitate.

TABLE II

Evaluation of some mercuric compounds.

(Heated for 5 hours)

Mercuric compound.	Hg present	% Mercury found by Gravimetric	% Error.	Volumetric	% Error.
1. Acetate	254 mg.	256 mg.	+0.8	255 mg	+0.4
2. Nitrate (in dil. HNO_3)	457	454	−0.7	456	−0.4
3. Perchlorate (in dil. $HClO_4$)	323	320	−1.0	320	−1.0
4. Phosphate (in dil. HCl)	182	180	−1.0	181	−0.5
5. Iodide (as K_2HgI_4)	360	353	−2.0	354	−1.8
6. Cyanide (in water)	201		No action		

Volumetric Method involving Direct Thiocyanate Titration.—Instead of weighing the mercury obtained in all the experiments, mentioned in this paper, it was found that it could also be estimated volumetrically after dissolving it in hot concentrated nitric acid. The dissolution was brought about in the sintered crucible itself. The solution and the washings were collected and evaporated to about 20 c.c. and then titrated with 0.1*N* ammonium thiocyanate solution in presence of ferric alum (Scott, *loc. cit.*, p. 581). The concentration of the mercury solution is important, as very dilute solutions are found to yield low values. The results of estimations made by this procedure are shown in Table II (under volumetric).

The dissolution of mercury in nitric acid was found to be quick when the metal was in the state of a fine powder. This was achieved specially in mercuric chloride solutions by adding about half a gram of potassium perchlorate to the reaction mixture.

Interferences.—Iron, cadmium and bismuth were found to interfere as they formed precipitates when weakly acidic solutions were treated with excess of sodium formate. Zinc, aluminium, lead and silver did not interfere provided that the solutions were prepared in dilute hydrochloric acid (Zn and Al) or in dilute nitric acid (Pb and Ag). Mixtures of lead and mercuric nitrates were estimated by a process similar to that described in connection with mercuric nitrate solution, except for the addition of potassium chloride, which was avoided as it gave a precipitate of lead chloride. The reduction of mercuric nitrate was found to progress through mercurous nitrate to metallic mercury. Lead nitrate remained unreduced. The results obtained gravimetrically agreed with the thiocyanate method and the error did not exceed 1%.

Mixtures of mercuric and silver nitrates in dilute nitric acid, when heated with sodium acetate and excess of sodium formate for 5 hours in a closed flask, gave an amalgam of silver and mercury. The silver salt was also reduced, probably quantitatively, to metallic silver. The amalgam was filtered through a G4 sintered crucible, well washed with water and finally with acetone. It was dried by leaving it overnight in the open. The dry precipitate was in the form of a grey spongy solid,

provided that the silver content was more than 20% of the mercury present. This solid being non-adhering was easily and completely transferred to a silica crucible and heated gently in a fume cupboard over a Bunsen flame until the weight became constant. The loss in weight which was due to volatilisation of mercury was recorded. The heating was regulated so as to prevent the melting of silver. This method gave excellent results with a precision of 0.5% which was better than that obtained for mercuric nitrate alone. The amalgamation of mercury with silver seemed to prevent its volatilisation, and hence, afforded better results.

Discussion

This reduction process has one disadvantage, that it requires prolonged heating for about 5 hours, otherwise a part of the mercury remains in the mercurous state. Apart from this it has several advantages, specially in the assay of mercuric chloride solutions. The direct titration of mercuric salts with thiocyanate solution has numerous drawbacks. Apart from the interference produced by several other metals, it is inapplicable in presence of chlorides, bromides and phosphates (Karaoglanov, *Z. anal. Chem.*, 1943, **125**, 405). It also gives unreliable results when the mercury solution is very dilute. The present procedure overcomes these difficulties by precipitating the metal which may be weighed as such or dissolved in nitric acid and then titrated accurately with thiocyanate solution. Moreover, it is also applicable in presence of silver and lead, which interfere with several methods available for mercury estimation.

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THE LIGHT SCATTERING BEHAVIOUR OF THORIUM ARSENATE GEL-FORMING SYSTEMS

By K. E. Jabalpurwala and D. M. Desai

The changes in the depolarisation and the intensity of transversely scattered light and opacity of thorium arsenate gels, obtained by diluting acid solution of thorium arsenate, have been investigated. The results show that the colloidal particles formed by diluting acid solution of thorium arsenate become hydrated and the gels are formed. During gelation there are no changes in the size and shape of the particles The gel particles, which are anisotropic and comparable with the wave-length of light used, seem to be disc-shaped.

Thorium arsenate gels are known to be formed either by metathesis between potassium arsenate and thorium nitrate or by diluting an acid solution of thorium arsenate. The literature reveals that gels formed by the former technique have received good attention, whereas those arising out of the latter method have escaped attention. It was therefore thought worth-while to study the optical properties of thorium arsenate gel-forming systems formed by diluting acid solution of thorium arsenate.

Experimental

Thorium arsenate was prepared by adding an excess of potassium arsenate to a solution of thorium nitrate and washing the gelatinous precipitate free of impurities by hot distilled water and drying in an air-oven at 110°. Thorium arsenate (30 g.) was then dissolved in 2.926*N*-HCl (250 c.c.). Thoria content was found to be 3.14%. A known volume of this solution, when diluted to different extents with distilled water, gave transparent to translucent gels.

Depolarisation factors of the transversely scattered light were measured by Cornu's method, taking all the necessary precautions.

The intensity of transversely scattered light was measured by a photoelectric method using a photomultiplier tube. The details of the circuit arrangement are given in a recent publication (cf. Sundaram and Desai, *Proc. Nat. Inst. Sci.*, 1954, **20**, 597).

The opacity of the gel-forming mixture was measured by using the Klett-Summerson photoelectric colorimeter. Distilled water was taken as blank.

The solutions used for preparing the gel-forming mixtures were made dust-free by repeated filtration through sintered glass filters.

The results obtained for the depolarisation values and the intensity as well as opacity measurements for gel-forming mixtures containing 4 c.c. of thorium arsenate solution, diluted to 52 c.c. or 72 c.c., are shown in Tables I and II. The following notations have been used in these tables.

T = time (min.) from the commencement of dilution of the acid solution.

t = time of setting of gel (min.).

O and I = opacity and intensity readings measured in arbitrary units.
The depolarisation values ρ_u, ρ_v, ρ_h are expressed as percentages.

TABLE I

Thorium arsenate = 4.0 c.c. Total volume = 52.0 c.c. t = 4 mins.

T.	ρ_u.	ρ_v.	ρ_h.	I.	O.	$I_{45°}/I_{135°}$.
1	3.80	1.30	...	8.0	0.0	4.0
2	3.80	...	59.95	8.0	0.0	4.0
3	3.82	1.30	59.95	9.0	1.0	4.10
4	3.96	...	...	11.5	7.5	...
5	4.14	1.30	56.79	12.0	12.0	4.08
7	4.14	...	...	13.0	19.0	...
10	4.33	1.30	...	15.5	26.5	4.12
15	...	...	49.03	19.0	37.0	...
20	4.52	1.30	...	22.5	46.0	4.48
25	4.71	...	...	25.0	51.5	...
30	...	1.40	46.36	26.5	55.0	4.60
40	4.71	...	...	32.0	62.5	...
60	...	1.51	...	36.5	67.5	4.63
80	4.92	...	44.65	40.0	72.0	...
100	4.92	1.51	43.81	40.5	73.5	4.68

TABLE II

Thorium arsenate = 4.0 c.c. Total volume = 72.0 c.c. t = 10 mins.

T.	ρ_u.	ρ_v.	ρ_h.	I.	O.	$I_{45°}/I_{135°}$.
1	2.80	1.11	...	7.0	0.0	3 80
2	2.80	1.11	64.58	7.0	0.0	...
3	2.80	...	...	7.0	0.0	...
4	2.80	1.11	64.58	7.0	0.0	...
5	2.80	1.11	64.58	7.0	0.0	3.80
7	2 80	...	...	7.0	0.0	...
9	2.80	1.11	...	7.5	1.5	...
10	2.95	...	63.27	8.0	2.0	3.96
15	...	1.20	...	8.5	6.5	...
25	3.11	...	61.04	10.0	14.0	4.11
30	3.27	1.30	...	10.0	15.5	...
40	3.27	...	59.95	10.5	18.5	4.23
60	3.43	...	...	11.0	22.0	...
80	...	1.40	57.82	12.5	24.0	4.30
100	3.61	1.40	56.79	13.5	25.0	4.32

DISCUSSION

Depolarisation Measurements.—It will be observed from the results recorded in Tables I and II that till about the gelation time, the values of ρ_u, ρ_v and ρ_h remain almost constant. It is further noticed that in these systems the values of ρ_u, ρ_v and ρ_h begin to change from near about the setting time and that these changes continue until they become almost constant. Since the values of ρ_u, ρ_v and ρ_h remain constant during the process of gel-formation, it may be concluded that there are no perceptible changes in the size and shape of the colloidal particles during the process of gel-formation. The departure from the zero value of ρ_v in these gels suggests that the gel-particles are anisotropic. The low values of ρ_h in these gels reveal that the particles are not very small as compared to the wave-length of light. The values of ρ_u, ρ_v and ρ_h seem to undergo continuous changes from just near about the setting time. From the study of their actual values it is clear that the particles in the set gels begin to grow in size and increase in anisotropy.

It has been reported (cf. Prasad and Guruswamy, *Proc. Indian Acad. Sci.*, 1944, **19A**, 66; Desai and Sundaram, *loc. cit.*; *J. Univ. Bombay*, 1954, **23**, 9) that in the gel-forming systems of thorium arsenate, formed by metathetical reaction, the colloid particles increase in size and anisotropy during gelation and that these changes continue even after the gels have set. From the increase in the values of I_0 they have concluded that the process of gel-formation, as revealed by the study of thorium arsenate, is analogous to coagulation.

Opacity and Intensity Measurements.—The changes in the values of opacity and intensity of transversely scattered light during and after the process of gel-formation are recorded in Tables I and II. It will be seen that the values of opacity and intensity are almost constant till about the setting time and thereafter there is a continuous increase in opacity and intensity, and that they tend to approach constant values. Similar changes have been observed for the intensity of light scattered in the forward and backward directions. These results indicate that there are no changes in the size, shape and/or number of gel-forming particles and that hydration does not affect opacity and intensity values. The increase in the values of opacity and intensity from near about the setting point suggests that in the freshly prepared thorium arsenate gels, there are changes in the size, shape and/or number of gel particles during the process of ageing. These observations, thus, support the conclusions drawn from the measurements of depolarisation factors.

Density and Anisotropy Scatterings.—The density and the anisotropy scatterings have been separately calculated for one system by using the equations,

$$I_D = I.\frac{6-7\rho}{6+6\rho} \quad \text{and} \quad I_A = I - I_D$$

where I_D = density scattering and I_A = anisotropy scattering, from the values of the intensity and depolarisation factors of the transversely scattered light and the values thus obtained are shown in Table III.

TABLE III

Thorium arsenate = 4 c.c. Total volume = 52.0 c.c.

T.	ρ_v.	$\rho = \frac{2\rho_v}{1+\rho_v}$.	$\frac{6-7\rho}{6+6\rho}$.	$I_{90}°$.	$I_h = I_{90}° \cdot \frac{6-7\rho}{6+6\rho}$.	$I_A = I_{90}° - I_h$.
1 mm.	1.30	0.0257	0.9442	8.0	7.55	0.45
2	1.30	0.0257	0.9442	8.0	7.55	0.45
3	1.30	0.0257	0.9442	9.0	8.50	0.50
4	1.30	0.0257	0.9442	11.5	10.86	0.60
5	1.30	0.0257	0.9442	12.0	11.33	0.67
7	1.30	0.0257	0.9442	13.0	12.27	0.73
10	1.30	0.0257	0.9442	15.5	14.64	0.86
20	1.30	0.0257	0.9442	22.5	21.24	1.26
30	1.40	0.0276	0.9418	26.5	24.96	1.54
60	1.51	0.0298	0.9373	36.5	34.21	2.29
80	1.51	0.0298	0.9373	40.0	37.49	2.51
100	1.51	0.0298	0.9373	40.5	37.96	2.54

As there are practically no changes in the values of I_h and I_A during gelation, it may be concluded that during this process there are no changes in the size, number and shape of the colloid particles. It is seen further that the scattering intensity is mostly due to density scattering in the initial stages and that throughout the process of ageing, the density scattering predominates over the anisotropy scattering.

Dissymmetry Ratio $I_{45}°/I_{135}°$.—In order to get some idea about the gel particles in the systems investigated, the ratio $I_{45}°/I_{135}°$ has been calculated from the measurements of the intensity of scattered light in the forward and backward directions and the results are shown in Tables I and II.

It is seen from the tables that the values of this ratio continuously increase only from about the gelation time and that it attains constant values sometime after the setting of gels, which indicate the increase in the size of the particles during ageing. The value of the ratios in fresh gels appears to be approximately 4. In the gel-systems studied in the present investigation, the particle size is fairly large, as can be inferred from the low values of ρ_h in the gel state. Although in gel-systems the particles cannot be considered to be independent of each other, yet from the values of the dissymmetry ratio one may infer that the particles in the thorium arsenate gels are probably disc-shaped. This conclusion is in harmony with the one drawn by Desai and Sundaram (*loc. cit.*) in the case of thorium arsenate gel-systems formed by metathetical reaction.

Effect of Dilution.—Tables I and II show that the values of ρ_h and ρ_v are relatively low for the gel containing greater amount of distilled water, that is, in less acidic medium. The values of ρ_h in the system containing greater amount of distilled water are relatively high. This means that in more dilute system the gel particles are relatively small and less anisotropic. This may probably be due to the formation of smaller and less anisotropic aggregates in loose systems wherein the amount of water seems to be more than what is required for the hydration of colloid particles.

The higher rate of change in opacity and in intensity of scattered light in the relatively less dilute system may be similarly accounted for.

Mechanism of Gel-formation.—When an acid solution of thorium arsenate is suitably diluted, thorium arsenate is thrown out because of the reduction in its solubility in the diluted acid. These particles then are held in colloid dimensions, as can be inferred from the depolarisation data. These particles then become heavily hydrated with the formation of the gels. During gelation there are practically no changes in size and shape of the colloid particles This is revealed by the measurement of the deplorisation factors, intensity and opacity of these systems during gelation.

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CHEMICAL INVESTIGATION ON THE LEAVES OF *GYMNEMA SYLVESTRE* R. Br.

By Hari Narayan Khastgir, Sudhendu Kumar Sengupta and Pasupati Sengupta

Lupeol, β-amyrin, stigmasterol and an amorphous antisaccharine principle have been isolated from the leaves of *Gymnema sylvestre* R. Br.

The leaves of *Gymnema sylvestre* R. Br. (Sanskrit: Meshashringi) of N.O. Asclepiadaceae possess antisaccharine property and are used in the Ayurvedic system of medicine as an antidiabetic agent. In a recent review Mukerji (*J. Sci. Ind. Res.*, 1957, **16A**, 477) has given an account of the medicinal use and the antisaccharine property of the plant along with the past chemical investigations carried out with it. Although considerable amount of investigations have been carried out with the leaves of the plant, still no crystalline compound except cyclitol (Posternak and Schopfer, *Helv. Chim. Acta*, 1950, **23**, 343) and tartaric acid (Chopra, "Indigenous Drugs of India," Art Press, Calcutta, 1933, p. 320) has been characterised. It is also not certain whether the amorphous substance, described as gymnemic acid (see above reference) by Hooper is a single substance or not. Further, Hooper's claim that gymnemic acid constituted the antisaccharine principle of the leaves has been challenged (Power and Tutin, *Pharm. J.*, 1904, **89**, 234; Chopra *et al.*, *Indian J. Med. Res.*, 1928, **16**, 115).

Because of its medicinal importance, we became interested in a systematic investigation of the leaves of the plant. The dried and powdered leaves were first extracted with petroleum ether (b.p. 60-80°) to give a brown resinous mass. After repeated chromatography and crystallisation we have been able to isolate from this resinous mass the triterpene alcohols, lupeol and β-amyrin and the plant sterol, stigmasterol. It may be pointed out, however, that if lupeol and β-amyrin, occur together in the same plant, it is extremely difficult to separate them. In fact, scandol, m.p. 161-63°, $[\alpha]_D$ + 56°.9, once believed to be a triterpene alcohol (Simonsen, "Terpenes", The University Press, Cambridge, 1957, Vol. IV, p. 442) has recently been proved to be an intimate mixture of lupeol and β-amyrin (Corey, Proskow and Parks, *J. Amer. Pharm. Assoc.*, 1957, **46**, 183).

After extraction with petroleum ether, the leaves were extracted with 95% ethyl alcohol. This extraction gave a water-soluble, brown, viscous gum which was partitioned between water and a mixture of chloroform and ethanol (2 : 1), when the chloroform-ethanol solution extracted the antisaccharine principle of the leaves. The antisaccharine principle, obtained as an amorphous powder, has so far resisted all attempts at crystallisation. Further investigations on this antisaccharine principle is in progress.

EXPERIMENTAL

Extraction and Chromatography.—Dried and powdered leaves of *Gymnema sylvestre* R. Br. (600 g) were extracted in a Soxhlet apparatus with petroleum ether (b.p. 60-80°) for 8 hours. The solvent was distilled off, leaving a brown resinous mass (14.5 g.), which was chromatographed over 500 g. of alumina and the following broad fractions were collected :

Fraction I	Petroleum ether eluate with increasing proportion of benzene up to petroleum ether : benzene (1 : 1) eluate.	Waxy matetial, 6 g.
Fraction II.	Benzene eluate.	Partially solid material, 2.6 g.
Fraction III.	Benzene : ether (1 : 1) eluate.	Partially solid material, 1.4 g.

Further elution with more polar solvents did not yield any crystalline material.

Fraction II : *Isolation of Lupeol and β-Amyrin Acetate* —Fraction II (2.6 g.) was chromatographed over 200 g. of activated alumina and after a forerun of 1.1 g. of a gummy material, petroleum ether-benzene (3 : 2) eluate gave two fractions : (A) 0.19 g. of a crystalline solid, m.p. 160-185°, followed by (B) 0.32 g. of a crystalline solid, m.p. 140-60°.

Lupeol.—Fraction A on repeated crystallisation from methanol and then from acetone gave colorless crystals, m.p. 212-13°, $[\alpha]_D$ +27°.7. The mixed m.p. with an authentic sample of lupeol did not show any depression.

Lupeol Acetate.—The above solid, m.p. 212-13°, was treated with acetic anhydride and pyridine as usual, when lupeol acetate crystallised from the reaction medium. The crystals were filtered and recrystallised from acetone. The analytical sample melted at 214-15°, $[\alpha]_D$ +47°.6. The melting point was not depressed when mixed with an authentic sample of lupeol acetate. (Found : C, 82.32 ; H, 10.95. Calc. for $C_{32}H_{52}O_2$: C, 81.99 ; H, 11.12%).

β-Amyrin Acetate.—Fraction B (0.32 g.) in the above chromatogram was repeatedly crystallised from methanol and then from acetone, when 0.18 g. of colorless crystals, m.p. 164-66°, $[\alpha]_D$ +51° (see scandol in the theoretical portion) were obtained. The crystals were acetylated with acetic anhydride and pyridine as usual, when an acetate crystallised out from the reaction medium. It was filtered and crystallised from acetone, when colorless crystals, m p. 236-38°, $[\alpha]_D$ +84°.8, were obtained. This acetate did not depress the melting point of an authentic sample of β-amyrin acetate. (Found : C, 81.81 ; H, 10.87. Calc. for $C_{32}H_{52}O_2$: C, 81.99 ; H. 11.12%).

Fraction III : *Isolation of Stigmasterol.*—Fraction III (1.4 g.) was rechromatographed over 50 g. of alumina when the benzene eluate gave 0.32 g. of a solid material, which on repeated crystallisation from methanol and then from acetone gave colorless crystals, m.p. 165-70°, $[\alpha]_D$ −48°.3. The constants reported for stigmasterol (Fieser and Fieser, "Natural Products Related to Phenanthrene", Reinhold Publishing Corporation, New York, 1949, p. 95) are m.p. 170° and $[\alpha]_D$ −49°.

Stigmasterol Acetate.—The above solid was converted into the acetate in the usual manner. The acetate after crystallisation from methanol and then from acetone, melted at 142°, $[\alpha]_D - 54°$. The mixed m.p. with an authentic sample of stigmasterol acetate did not show any depression. (Found : C, 81.91 ; H, 10.95. Calc. for $C_{31}H_{50}O_2$: C, 81.88 ; H, 11.08%).

Stigmasterol benzoate was prepared in the usual manner, m.p. 159-60°, $[\alpha]_D - 27°$. (Found : C, 83.60 ; H, 9.92. Calc. for $C_{36}H_{52}O_2$: C, 83.66 ; H, 10.14%).

Isolation of the Amorphous Antisaccharine Principle.—Dried leaves of *Gymnema sylvestre* R. Br. (600 g.), after extraction with petroleum ether, were extracted in a Soxhlet apparatus with 95% ethyl alcohol for 24 hours. The solvent was removed and the brown viscous gum was dissolved in 100 c.c. of water and extracted with ether. The aqueous solution was then extracted thrice with 100 c.c. portions of a mixture of chloroform and ethanol (2 : 1). The combined chloroform-ethanol solution was once washed with 50 c.c. water, dried over anhydrous sodium sulphate and evaporated. The amorphous residue, thus obtained, was taken up in methanol, charcoaled and evaporated, when 8.5 g. of the amorphous antisaccharine principle was obtained. The solid lost the antisaccharine property in contact with aqueous hydrochloric acid and precipitated another amorphous substance, presumably the gymnemic acid of Hooper. The antisaccharine principle was chromatographed over silica gel. But all attempts at crystallisation have failed so far.

The authors are indebted to Dr. (Mrs.) Asima Chatterjee, Reader in Chemistry, Calcutta University, for the authentic samples of lupeol and lupeol acetate and to Dr. B. K. Bhattacharyya, Professor of Organic Chemistry, Jadavpore University, for the authentic sample of β-amyrin acetate. They are also indebted to Mr. Priyalal Moulik for the optical rotation study of the compounds and to Mr. N. C. Guha, Research Director, E. I. P. W. Ltd., for his kind suggestions and encouragement.

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CHEMISTRY OF BERYLLIUM. PART III. COMPOUNDS OF BERYLLIUM CHLORIDE WITH AMINOPHENOLS, AMINOBENZOIC ACIDS, *p*-NITROANILINE AND 2 : 4-DINITROPHENYLHYDRAZINE

By Sarju Prasad and Kashi Prasad Srivastava

Complex compounds of aminophenols, aminobenzoic acids, *p*-nitroaniline and 2 : 4-dinitrophenylhydrazine with beryllium chloride have been prepared and their constitution discussed. Salts of the complexes of aminophenols and aminobenzoic acids have been prepared.

A survey of literature shows that no work has been done on the complex formation of beryllium chloride with aminophenols, aminobenzoic acids, *p*-nitroaniline and 2 : 4-dinitrophenylhydrazine. The present work was therefore undertaken with a view to studying the formation of complex compounds of beryllium chloride with these substances. Beryllium salts of the amino acids and aminophenols were also prepared.

Experimental

Anhydrous beryllium chloride was prepared by the method of Pollok (*J. Chem. Soc.*, 1904, **85**, 603). Excess of chlorine was removed by passing dry carbon dioxide. It was extracted with ether, dehydrated over sodium.

Two types of complexes, (A) addition and (B) addition-cum-substitution, have been prepared.

(*A*) *Addition Complexes*

On mixing separately ethereal solution of beryllium chloride with aminophenols, aminobenzoic acids and *p*-nitroaniline, complex compounds separated out immediately. The precipitate was allowed to settle and the supernatant liquid decanted through a dry filter paper. The precipitate was repeatedly washed with dry ether till the filtrate did not respond to tests of the reactants. The precipitate was then transferred to the filter paper, filter-pressed and finally dried in vacuum.

The complex compound with *m*-aminobenzoic acid was also prepared by suspending the acid in minimum quantity of absolute alcohol and then adding an ethereal solution of $BeCl_2$. The complex formed dissolved, leaving behind the excess acid; the mixture was allowed to stand for an hour with frequent shaking and filtered. The filtrate on evaporation gave the pure compound.

In the case of nitroaniline, only half of the complex compound separated out. On evaporating the filtrate, a yellow compound was obtained which on further purification by repeated washings with dry benzene gave a similar compound.

Compounds with 2:4-Dinitrophenylhydrazine.—2:4-Dinitrophenylhydrazine was taken in a glass-stoppered conical flask, cooled in ice and an excess of ethereal solution of $BeCl_2$ added (1:1 ratio). The mixture was allowed to stand in ice for an hour with frequent shaking after which it was brought to the room temperature and shaken well for about 2 hours. Nearly 10 c.c. of $BeCl_2$ solution (1.6 g./100 c.c. ether) was again added and the mixture shaken well for some time and then left overnight. The compound obtained was purified by repeated washing with dry ether. It was filter-pressed and dried in vacuum.

In a second experiment, dinitrophenylhydrazine was mixed with an ethereal solution of $BeCl_2$ in the ratio of 1:2. Ether was distilled off and the reaction mixture was heated on a water-bath for an hour to complete the reaction. It was cooled and the reaction product was repeatedly washed with dry ether and dried in vacuum.

In another experiment, the temperature was slowly raised to study the compound formed at the melting point of dinitrophenylhydrazine, but there was a violent reaction between 130° and 140° and the mixture was charred. A similar violent reaction took place when dry $BeCl_2$ and dinitrophenylhydrazine were heated together.

(*B*) *Addition-cum-Substitution Complexes*

Preparation of Salts of the Aminophenol and Aminobenzoic Acid Complexes.—Salts of aminophenol or amino-acid complexes were prepared by adding an ethereal solution of $BeCl_2$ (in slight excess of that theoretically required) to a weighed quantity of the complex. The mixture was slowly heated in an oil-bath to remove ether and the temperature was raised and maintained at 10-15° above the m.p. of the respective phenol or acid. When the evolution of HCl had ceased, the flask was cooled and the mixture was washed repeatedly with dry ether till free of $BeCl_2$. The compound obtained was filter-pressed and finally dried in vacuum. All the above reactions were carried out in the absence of moisture.

A weighed quantity of the substance was treated with dilute NaOH solution, boiled, and then neutralised with dilute HCl till slightly acidic. Beryllium was precipitated as $Be(OH)_2$ and washed free of electrolyte with 2% ammonium acetate solution. $Be(OH)_2$ was dissolved in dilute HCl, reprecipitated as hydroxide, washed free of electrolyte as before, dried, ignited and weighed as BeO.

Chlorine was determined by Piria and Schiff's method and nitrogen by Kjeldahl's method (except in the case of compounds containing $-NO_2$ groups).

General Properties.—All the compounds prepared are coloured, insoluble in benzene, carbon tetrachloride, ether (except the compound obtained with nitroaniline which is partially soluble), petroleum ether but soluble in alcohol. The compound obtained with *m*-aminobenzoic acid is soluble in water. Compounds obtained with 2:4-dinitrophenylhydrazine change colour from chocolate-brown to orange-red when exposed to atmosphere.

TABLE I

Compounds of $BeCl_2$ with aminophenols, aminobenzoic acids, nitroaniline and 2 : 4-dinitrophenylhydrazine.

	Organic compounds used.	% Beryllium. Found.	Calc.	% Chlorine. Found.	Calc.	% Nitrogen. Found.	Calc.	Colour.	Compound.
1.	*o*-Amino-phenol	3.04	3.02	23.91	23.82	9.20	9.34	Dark brown	$BeCl_2.2C_6H_4OHNH_2$
2.	*m*-Amino-phenol	3.03	3.02	23.88	23.82	9.22	9.34	Ash	$BeCl_2.2C_6H_4OHNH_2$
3.	*o*-Amino-benzoic acid	2.52	2.54	20.05	20.06	7.84	7.91	Light pink	$BeCl_2.2C_6H_4COOH.NH_2$
4.	*m*-Amino-benzoic acid	2.53	2.54	20.05	20.06	7.87	7.91	Brown	$BeCl_2.2C_6H_4.NH_2COOH$
5.	*p*-Nitro-aniline	2.52	2.53	19.99	19.94	...	...	Yellow	$BeCl_2.2C_6H_4NO_2.NH_2$
6.	2 : 4-Dinitro-phenyl-hydrazine	1.92	1.89	14.95	14.91	...	...	Chocolate	$BeCl_2.2C_6H_3(NO_2)_2NH.NH_2$
7.	"	3.25	3.23	25.57	25.57	...	...	"	$BeCl_2.C_6H_3(NO_2)_2NH.NH_2$

TABLE II

Salts of the aminophenol and aminobenzoic acid complexes.

	Complex compound.	% Beryllium. Found.	Calc.	% Chlorine. Found.	Calc.	% Nitrogen. Found.	Calc.	Colour.	Compound.
1.	*o*-Amino-phenol	5.97	5.90	23.19	23.28	9.06	9.18	Black	$Be_2Cl_2.2C_6H_4O.NH_2$
2.	*m*-Amino-phenol	5.94	5.90	23.23	23.28	9.10	9.18	Dark ash	$Be_2Cl_2.2C_6H_4O.NH_2$
3.	*o*-Amino-benzoic acid	5.03	4.99	19.52	19.66	7.56	7.76	Light ash	$Be_2Cl_2\ 2C_6H_4COO.NH_2$
4.	*m*-Amino-benzoic acid	5.03	4.99	19.50	19.66	7.58	7.76	Light brown	$Be_2Cl_2.2C_6H_4COO.NH_2$

DISCUSSION

From the results it is evident that two molecules each of aminophenols, aminobenzoic acids, *p*-nitroaniline and 2 : 4-dinitrophenylhydrazine combine with one molecule of beryllium chloride in the cold to yield the complex compounds which are similar to those obtained with aromatic amines (Prasad and Srivastava, this *Journal*, 1957, **34**, 317). These can be represented as:

(*i*)
$$\begin{matrix} C_6H_4OH.NH_2 \\ C_6H_4OH.NH_2 \end{matrix} \searrow\nearrow Be \begin{matrix} Cl \\ Cl \end{matrix}$$

in the case of aminiphenol and

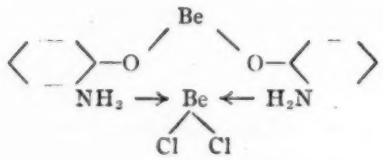
(*ii*)
$$\begin{matrix} C_6H_4COOH.NH_2 \\ C_6H_4COOH.NH_2 \end{matrix} \searrow\nearrow Be \begin{matrix} Cl \\ Cl \end{matrix}$$

in the case of amino-acids. The hydroxyl, carboxyl, nitro- and *sec.*-NH groups do not co-ordinate in the presence of a strong donor group like $-NH_2$. A similar result was obtained in the case of *p*-aminodiethylaniline (Prasad and Srivastava, *loc. cit.*).

Fricke and Havestadt (*Z. anorg. Chem.*, 1925, **148**, 157) observed that phenylhydrazine and hydrazine formed two compounds, viz , $BeCl_2.3Ph.NH.NH_2$ and $BeCl_2.4Ph.NH.NH_2$, in which beryllium exibited a co-ordination number of six and eight respectively. It is interesting to note that one molecule of $BeCl_2$ combines with two molecules of dinitrophenylhydrazine in the cold and with one molecule at 100°. When the temperature is further raised, a violent reaction takes place at 130-40° and the mass chars.

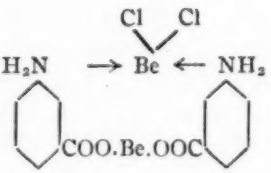
Complex compounds obtained with *o*- and *m*-aminophenols and *o*- and *m*-aminobenzoic acids react readily with $BeCl_2$ when heated at a temperature slightly higher than the melting point of the respective phenol or acid. A substitution reaction takes place and hydroxyl or carboxyl group present reacts with $BeCl_2$, when a salt of the complex is formed with evolution of HCl gas. The reactions can be represented as :

(*i*) $BeCl_2.2C_6H_4OH.NH_2 + BeCl_2 \rightarrow$



in the case of *o*-aminophenol and

(*ii*) $BeCl_2.2C_6H_4.NH_2COOH + BeCl_2 \rightarrow$



in the case of *m*-aminobenzoic acid.

In all the cases studied (vide Table II), the percentage of beryllium is slightly higher than the theoretical, showing thereby that the complex compounds undergo a slight decomposition, when heated.

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BENZYLTHIOUREAS. PART II

By J. P. Trivedi and J. J. Trivedi

Several monosubstituted benzylthioureas and 1-(*p*-substituted benzyl)-3-(*p*-*n*-alkoxyphenyl)- and -3-(*p*-dimethylaminophenyl)-thioureas have been synthesised.

In continuation of our previous work (Shah, Trivedi and Trivedi, this *Journal*, 1956, **33**, 423), several substituted thioureas have been described in the present communication. Huebner *et al.* (*J. Amer. Chem. Soc.*, 1953, **75**, 2274) reported the high antitubercle activity of 4:4′-disubstituted thiocarbanilides. 4-Ethoxy-4′-dimethylaminothiocarbanilide exceeded the activity of PAS and streptomycin and approached that of isoniazide (Eisman *et al.*, *Am. Rev. Tubercle*, 1954, **70**, 121, 130).

p-Chlorobenzyl- and *p*-bromobenzyl-thioureas were found to show higher antibacterial and antifungal activity as compared to benzylthiourea (Miss Shah, Ph.D. thesis, Bombay Univ., 1957). This prompted us to prepare thioureas containing halogen- and alkoxy-substituted benzyl group as well as alkoxy and dimethylaminophenyl groups in the same molecule. With this end in view, 1-(*p*-chlorobenzyl)-3-(*p*-*n*-alkoxyphenyl)-, 1-(*p* bromobenzyl)-3-(*p*-*n*-alkoxyphenyl)-, 1-(*p*-*n*-alkoxybenzyl)-3-(*p*-*n*-alkoxyphenyl)- and 1-(*p*-dimethylaminophenyl)-3-(*p*-halogen- or alkoxy-substituted benzyl)-thioureas have been prepared and described in the present communication. A few methyl-, dimethyl- or methoxy-substituted benzylthioureas as well as α-phenylalkyl-thioureas have also been synthesised.

Experimental

Mono- and dimethyl substituted benzylamines were prepared from the corresponding substituted benzyl halides by the method of Graymore (*J. Chem. Soc.*, 1947, 1116).

Methoxybenzylamines were prepared from the corresponding aldehydes by the Leuckart reaction (Ettlinger and Lunden, *J. Amer. Chem. Soc.*, 1956, **78**, 1953). α-Phenylethyl-, α-phenylpropyl- and α-phenyl-*n*-butylamines were prepared by the Leuckart reaction of acetophenone, propiophenone and butyrophenone (Ingersoll, *ibid.*, 1936, **58**, 1808).

p-Ethoxy- and *p*-*n*-butoxybenzylamines were prepared by reduction of oximes of the corresponding aldehydes ("Org. synthesis", Coll. Vol. **11**, 1943, p. 318).

p-Aminophenyl alkyl ethers were prepared by reduction of *p*-nitrophenyl alkyl ethers, prepared according to Weygand and Gabler (*J. prakt. Chem.*, 1940, **155**, 132) and Gray and Jones (*J. Chem. Soc.*, 1954, 1469).

Amines were converted into *iso*thiocyanates in 60% yield according to the procedure described previously (*loc. cit.*). The *iso*thiocyanates prepared are described in Tables I and II.

TABLE I

Benzyl isothiocyanates.

$$X-C_6H_4\underset{\displaystyle R}{\underset{|}{C}}H-N=C=S$$

Compound. X=	R=	B.P.	Formula.	% Sulphur. Found.	Calc.
p-OC_2H_5	H	98°/5 mm	$C_{10}H_{11}ONS$	16.5	16.6
p-*n*-OC_4H_9	H	142-45°/10	$C_{12}H_{15}ONS$	14.2	14.5
o-CH_3	H	120°/7	C_9H_9NS	19.5	19.6
m-CH_3	H	148°/15	,,	19.5	,,
p-CH_3	H	155°/17	,,	19.5	,,
o-OCH_3*	H	132°/5-7	C_9H_9ONS	17 8	17.9
m-OCH_3	H	128°/3	,,	17.8	,,
p-OCH_3†	H	125°/7	...	...	...
2 CH_3 (3 : 4)	H	170°/12	$C_{10}H_{11}NS$	18.0	18.1
2 CH_3 (2 : 4)	H	120°/50	,,	18.0	,,
2 CH_3 (2 : 5)	H	160°/9	,,	18 0	,,
H	CH_3	140°/5	C_9H_9NS	19.6	19.6
H	C_2H_5	160°/3	$C_{10}H_{11}NS$	18.0	18.1
H	*n*-C_3H_7	130°/10	$C_{11}H_{13}NS$	16.7	16.7

* Kjaer *et al.*, *Acta Chem. Scand.*, 1956, **10**, 26.
† V. Braun *et al.*, *Ber.*, 1912. **45**, 2191.

TABLE II

p-n-*Alkoxyphenyl* isothiocyanates.

$$X-C_6H_4-N=C=S.$$

Compound X=	B.P.	Formula.	% Sulphur. Found.	Calc.
-OCH_3*	280°	...	...	...
-OC_2H_5†	(M.P.) 76°	...	...	...
n-OC_3H_7	160°/12 mm,	$C_{10}H_{11}ONS$	16.5	16.6
n-OC_4H_9	170°/15	$C_{11}H_{13}ONS$	15.1	15.4
n-OC_5H_{11}	170°/15	$C_{12}H_{15}ONS$	14.1	14.4
n-OC_6H_{13}	180°/7	$C_{13}H_{17}ONS$	13.1	13.6

* Dyson, *J. Chem. Soc.*, 1927, 443.
† Dyson, *ibid.*, 1927, 1705.

Substituted benzylthioureas, shown in Table III, were prepared as described previously (*loc. cit.*) ; yield 40 to 50%.

1-(*p*-Chlorobenzyl)-3-(*p*-*n*-alkoxyphenyl)-thioureas were prepared by condensation of *p*-chlorobenzyl *iso*thiocyanate with the corresponding *p*-*n*-alkoxy-anilines according to Buu-Hoï *et al.* (*J. Chem. Soc.*, 1955, 1573) in 60% yield

1-(*p*-Bromobenzyl)-3-(*p*-*n* alkoxyphenyl)-thioureas were prepared by condensation of *p*-bromobenzyl *iso*thiocyanate with the corresponding *p*-*n*-alkoxy-anilines according to Buu-Hoï *et al.* (*loc. cit.*) in 60% yield.

1-(*p*-Ethoxybenzyl)-3-(*p*-*n*-alkoxyphenyl)-thioureas and 1-(*p* *n*-butoxybenzyl)-3-(*p*-*n*-alkoxyphenyl)-thioureas were prepared by condensation of *p*-ethoxybenzyl *iso*-thiocyanate and *p*-*n*-butoxybenzyl *iso*thiocyanate respectively with the corresponding *p*-*n*-alkoxy-anilines according to Buu-Hoï (*loc. cit.*) in 60% yield.

1-(*p*-Substituted benzyl)-3-(*p*-dimethylaminophenyl)-thioureas were prepared by condensation of *p*-substituted benzyl *iso*thiocyanates with *p*-dimethylaminoaniline according to Buu-Hoï *et al.* (*loc. cit.*) in 60% yield. These compounds are described in Table IV.

TABLE III

Substituted benzylthioureas.

$$X-C_6H_4-\underset{\displaystyle R}{\underset{|}{CH}}-NHCSNH_2$$

Compound.		M.P.	Formula.	% Sulphur.	
X=	R=			Found.	Calc.
p-CH_3	H	106°	$C_9H_{12}N_2S$	17.4	17.8
2 CH_3 (3 : 4)	H	120°	$C_{10}H_{14}N_2S$	16.3	16.5
2 CH_3 (2 : 5)	H	110°	,,	16.4	,,
o-OCH_3	H	145°	$C_9H_{12}ON_2S$	16.1	16.3
m-OCH_3	H	102°	,,	16.3	,,
H	CH_3	147°	$C_9H_{12}N_2S$	17.7	17.8
H	C_2H_5	133°	$C_{10}H_{14}N_2S$	16.3	16.5
H	*n*-C_3H_7	98°	$C_{11}H_{16}N_2S$	15.2	15.4

TABLE IV

1-(p-*Substituted benzyl*)-3-(p-*substituted phenyl*)-*thioureas.*

$X-C_6H_4CH_2-NHCSNH-C_6H_4R.$

Compound. R=	X=	M.P.	Formula.	Found.	Calc.
$-OCH_3$	Cl	132°	$C_{15}H_{15}ON_2ClS$	Cl : 11.4%	11.6%
$-OC_2H_5$	Cl	148°	$C_{16}H_{17}ON_2ClS$	Cl : 11.0	11.1
n-OC_3H_7	Cl	120°	$C_{17}H_{19}ON_2ClS$	Cl : 10.5	10.6
n-OC_4H_9	Cl	110°	$C_{18}H_{21}ON_2ClS$	Cl : 9.9	10.2
n-OC_5H_{11}	Cl	86°	$C_{19}H_{23}ON_2ClS$	Cl : 9.7	9.8
n-OC_6H_{13}	Cl	92°	$C_{20}H_{25}ON_2ClS$	Cl : 9.2	9.4
$-OCH_3$	Br	147°	$C_{15}H_{15}ON_2BrS$	Br : 22.7	22.8
$-OC_2H_5$	Br	135°	$C_{16}H_{17}ON_2BrS$	Br : 21.9	21.9
n-OC_3H_7	Br	120°	$C_{17}H_{19}ON_2BrS$	Br : 20.9	21.1
n-OC_4H_9	Br	154°	$C_{18}H_{21}ON_2BrS$	Br : 20.1	20.3
n-OC_5H_{11}	Br	93°	$C_{19}H_{23}ON_2BrS$	Br : 19.6	19.6
n-OC_6H_{13}	Br	96°	$C_{20}H_{25}ON_2BrS$	Br : 18.7	19.0
$-OCH_3$	$-OC_2H_5$	113°	$C_{17}H_{20}O_2N_2S$	S : 10.0	10 1
$-OC_2H_5$	$-OC_2H_5$	98°	$C_{18}H_{22}O_2N_2S$	S : 9.6	9.7
n-OC_3H_7	$-OC_2H_5$	78°	$C_{19}H_{24}O_2N_2S$	S : 9.2	9.3
n-OC_4H_9	$-OC_2H_5$	83°	$C_{20}H_{26}O_2N_2S$	S : 8.9	8.9
n-OC_5H_{11}	$-OC_2H_5$	61°	$C_{21}H_{28}O_2N_2S$	S : 8.5	8.6
n-OC_6H_{13}	$-OC_2H_5$	56°	$C_{22}H_{30}O_2N_2S$	S : 8.2	8.3
$-OCH_3$	n-OC_4H_9	175°	$C_{19}H_{24}O_2N_2S$	S : 9.2	9.3
$-OC_2H_5$	n-OC_4H_9	96°	$C_{20}H_{26}O_2N_2S$	S : 8.9	8.9
n-OC_3H_7	n-OC_4H_9	85°	$C_{21}H_{28}N_2N_2S$	S : 8.6	8.6
n-OC_4H_9	n-OC_4H_9	71°	$C_{22}H_{30}O_2N_2S$	S : 8.1	8.3
n-OC_5H_{11}	n-OC_4H_9	135°	$C_{23}H_{32}O_2N_2S$	S : 7.9	8.0
n-OC_6H_{13}	n-OC_4H_9	73°	$C_{24}H_{34}O_2N_2S$	S : 7.6	7.7
$-N(CH_3)_2$	Cl	139°	$C_{16}H_{18}N_3ClS$	S : 10.0	10.0
$-N(CH_3)_2$	Br	148°	$C_{16}H_{18}N_3BrS$	S : 8.7	8.8
$-N(CH_3)_2$	$-OCH_3$	108°	$C_{17}H_{21}ON_3S$	S : 10.0	10.1
$-N(CH_3)_2$	$-OC_2H_5$	69°	$C_{18}H_{23}ON_3S$	S : 9.7	9.7
$-N(CH_3)_2$	n-OC_4H_9	120°	$C_{20}H_{27}ON_3S$	S : 8.9	8.9

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BARBITURATES. PART I. 5:5-DIETHYL-N^1-(SUBSTITUTED BENZYL) AND N^1-(SUBSTITUTED PHENYL) BARBITURATES AND THIOBARBITURATES

By J. P. Trivedi and J. J. Trivedi

Several N^1-substituted benzyl-5 :5-diethyl barbiturates and thiobarbiturates have been prepared and described.

Barbiturates have been studied very extensively. 5 : 5-Diethyl barbiturate, Veronal, was the first barbiturate used as a hypnotic (Fischer and Von Mering, *Therap. Gegenwart.*, 1903, **44**, 97). 5-Ethyl-5-phenyl barbiturate, Luminal, was introduced as an anticonvulsant by Hauptman (*Munch. med. Wochschr.*, 1912, **59**, 1907) in the treatment of epilepsy. 5-Ethyl-5-(1-methylbutyl)-2-thiobarbituric acid, Pentothal, and 5-ethyl-5-*iso*amyl-2-thiobarbituric acid, Thioethamyl, are useful as general anesthetics (Volwiller, *J. Amer. Chem. Soc.*, 1935, **57**, 1961). Kushner *et al.* (*J. Org. Chem.*, 1951, **16**, 1283) found Hibicon, *N*-benzyl-β-chloropropionamide, useful in grand mal epilepsy. N^1-alkylation of barbiturates makes them more useful in epileptic conditions. Mebaral, 1-methyl-5-ethyl-5-phenyl barbiturate, is an useful anticonvulsant. *N*-alkyl derivatives of substituted succinimides have also been found to exhibit anticonvulsant properties (Miller *et al.*, *J. Amer. Chem. Soc.*, 1951, **73**, 4895 ; 1953, **75**, 6256).

It was considered of interest to synthesise barbiturates containing substituted benzyl group on the nitrogen atom. 5 : 5-Diethyl-N^1-(substituted benzyl) barbiturates and thiobarbiturates have been synthesised and described in the present communication. For comparison some N^1-substituted-phenyl thiobarbiturates have also been prepared.

Barbiturates were synthesised by the condensation of diethyl ethylmalonate and the substituted benzylureas and thioureas in presence of sodium ethoxide.

Experimental

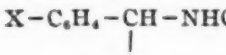
Substituted benzylureas were prepared from the corresponding amines and potassium cyanate in presence of an acid. The hitherto-unknown substituted benzylureas are shown in Table I. Substituted benzylthioureas were prepared as described previously (Shah, Trivedi and Trivedi, this *Journal*, 1956, **33**, 423 ; Trivedi and Trivedi, *ibid.*, 1958, **35**, 657). Diethyl ethylmalonate was prepared by the standard method (Wallingford and Jones, *J. Amer. Chem. Soc.*, 1942, **64**, 578).

Condensation of Diethyl Ethylmalonate with Substituted Ureas and Thioureas.— To a solution of sodium ethoxide, prepared from sodium (0.2 g. atom) and absolute ethanol (70 c.c.), was quickly added, with shaking, diethyl ethylmalonate (0.05 *M*), followed by appropriate substituted urea (0.05 *M*) or thiourea (0.06 *M*). The reaction mixture was then refluxed at 120° for 8 to 10 hours, the excess of alcohol distilled off, and the mixture diluted with 100 to 120 c.c. of water. It was filtered off and the filtrate after acidifying and keeping overnight deposited the barbituric acids. These were crystallised from alcohol or benzene ; yield 25 to 30%.

N^1-(Substituted benzyl)-5 : 5-diethyl barbiturates, thus prepared, are shown in Table II. N^1-(Substituted benzyl)-5 : 5-diethylthiobarbituric acids prepared are shown in Table III and N^1-substituted phenyl-2-thiobarbituric acids are shown in Table IV.

TABLE I

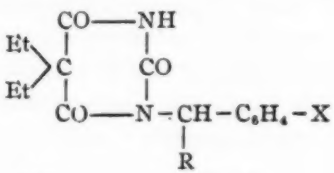
Substituted benzylureas.



Compound.		M.P.	Formula.	% Nitrogen.	
				Found.	Calc.
X =	R =				
o-Cl	H	143°	$C_8H_9ON_2Cl$	15.1	15.2
p-Cl	H	122°	,,	12.1	,,
o-Br	H	162°	$C_8H_9ON_2Br$	12.2	12.2
p-Br	H	172°	,,	12.2	,,
2 Me (3 : 4)	H	164°	$C_{10}H_{14}ON_2$	15.6	15.7
2 Me (2 : 5)	H	196°	,,	15.7	,,
m-OMe	H	148°	$C_9H_{12}O_2N_2$	15.5	15.6
H	Et	104°	$C_{10}H_{14}ON_2$	15.7	15.7
H	*n*-Pr	116°	$C_{11}H_{16}ON_2$	14.5	14.6

TABLE II

N^1-(*Substituted benzyl*)-5 : 5-*diethylbarbituric acids.*



Compound.		M.P.	Formula.	% Nitrogen.	
				Found.	Calc.
X =	R =				
o-Cl	H	248°	$C_{15}H_{17}O_3N_2Cl$	9.0	9.1
p-Cl	H	134°	,,	9.0	,,
o-Br	H	120-21°	$C_{15}H_{17}O_3N_2Br$	7.9	7.9
m-Br	H	120°	,,	7.9	,,
p-Br	H	124°	,,	7.9	,,
o- Me	H	120°	$C_{16}H_{20}O_3N_2$	9.7	9.7
m-Me	H	106°	,,	9.7	,,
p- Me	H	117°	,,	9.7	,,
2 Me (3:4)	H	178°	$C_{17}H_{22}O_3N_2$	9.1	9.3
2 Me (2:4)	H	136°	,,	9.2	,,
2 Me (2:5)	H	267°	,,	9.2	,,
o- OMe	H	132-33°	$C_{16}H_{20}O_4N_2$	9.2	9.2
m-OMe	H	Wax-like	...	...	...
p- OMe	H	224-25°	$C_{16}H_{20}O_4N_2$	9.2	9.2
H	Me	90°	$C_{16}H_{20}O_3N_2$	9.6	9.7
H	Et	109°	$C_{17}H_{22}O_3N_2$	9.2	9.3
H	*n*-Pr	88°	$C_{18}H_{24}O_3N_2$	8.8	8.9

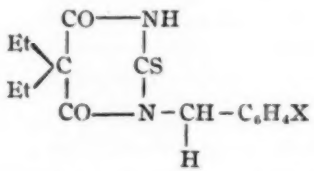
The two following phenylthioureas used for the preparation of N^1-(substituted phenyl)-2-thiobarbituric acids seem to be hitherto unknown.

p-n-Butoxyphenylthiourea, m.p. 158°. (Found : S, 14.1. $C_{11}H_{16}ON_2S$ requires S, 14.3%).

p-n-Hexyloxyphenylthiourea, m.p. 112°. (Found : S, 12.6. $C_{13}H_{20}ON_2S$ requires S, 12.7%).

TABLE III

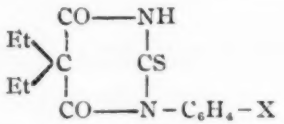
N^1-(Substituted benzyl)-5 : 5-diethyl-2-thiobarbituric acids.



Compound.		M.P.	Formula.	% Nitrogen.	
				Found.	Calc.
X=	R				
o-Cl	H	114°	$C_{15}H_{17}O_2N_2ClS$	8.6	8.6
m-Cl	H	118°	,,	8.6	,,
p-Cl	H	120°	,,	8.5	,,
o-Br	H	116°	$C_{15}H_{17}O_2N_2BrS$	7.5	7.6
m-Br	H	122°	,,	7.5	,,
p-Br	H	142°	,,	7.5	,,
o- Me	H	112-14°	$C_{16}H_{20}O_2N_2S$	9.1	9.2
m-Me	H	92°	,,	9.2	,,
p- Me	H	163°	,,	9.2	,,
2 Me (3:4)	H	179-80°	$C_{17}H_{22}O_2N_2S$	8.7	8.8
2 Me (2:4)	H	118°	,,	8.7	,,
2 Me (2:5)	H	116°	,,	8.8	,,
o- OMe	H	112°	$C_{16}H_{20}O_3N_2S$	8.7	8.8
m-OMe	H	117-18°	,,	8.7	,,
p-OMe	H	127-28°	,,	8.7	,,
H	Me	120°	$C_{16}H_{20}O_2N_2S$	9.2	9.2
H	Et	110°	$C_{17}H_{22}O_2N_2S$	8.8	8.8
H	*n*-Pr	112°	$C_{18}H_{24}O_2N_2S$	8.4	8.4

TABLE IV

5 : 5-Diethyl-N¹-(substituted phenyl)-2-thiobarbituric acids.



Compound.	M.P.	Formula.	% Nitrogen. Found.	Calc.
X=				
p−OCH_3	216°	$C_{15}H_{18}O_3N_2S$	10.3	10.3
p−OC_2H_5	200°	$C_{16}H_{20}O_3N_2S$	9.8	9.8
p−*n*-OC_3H_7	120°	$C_{17}H_{22}O_3N_2S$	9.3	9.4
p−*n*-OC_4H_9	115°	$C_{18}H_{24}O_3N_2S$	8.9	8.9
p−*n*-OC_5H_{11}	116°	$C_{19}H_{26}O_3N_2S$	8.5	8.6
p−*n*-OC_6H_{13}	130°	$C_{20}H_{28}O_3N_2S$	8.2	8.2
o− Cl	121°	$C_{14}H_{15}O_2N_2ClS$	9.0	9.0
m−Cl	183°	,,	,,	,,
p− Cl	212°	,,	,,	,,
m−Br	115°	$C_{14}H_{15}O_2N_2BrS$	7.8	7.9
p−Br	246°	,,	,,	,,

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POTENTIOMETRIC STUDIES ON THE COMPOSITION OF MANGANESE FERROCYANIDE COMPLEX

By Ram Sahai Saxena

The formation and composition of manganese ferrocyanide has been studied by potentiometric titrations between manganese chloride and potassium ferrocyanide, using ferricyanide-ferrocyanide electrode, both by the direct and the inverse methods. The equivalence point obtained from the maximum value of dE/dC corresponds to the formation of a compound having the composition $4Mn_2Fe(CN)_6 . 3K_4Fe(CN)_6$, with either of the substances used as the reagent. The titration curves have a regular form; there is a sharp break in potential at the equivalence point and the results are accurate and reproducible. The effect of varying concentrations of alcohol on the end-point as well as on the nature of the curves has been studied.

The reaction between manganese salt and $K_4Fe(CN)_6$ has been investigated by several workers by purely analytical methods and also by physico-chemical methods, but there is hardly any co-ordination of the views expressed by them. Stone and Van Ingen (*J. Amer. Chem. Soc.*, 1897, **19**, 542) observed that the composition of manganese ferrocyanide corresponded to $K_2MnFe(CN)_6$, when $K_4Fe(CN)_6$ was added to manganese salt and it changed to $K_4Mn_4[Fe(CN)_6]_3$, when precipitated in cold from an acid solution containing 5% HCl. Dickie (*ibid.*, 1902, **24**, 1023) analysed manganese ferrocyanide by precipitating the compound in neutral and acidic solutions and observed that the percentage of Mn increased in the compound by adding an excess of manganese salt to $K_4Fe(CN)_6$, but when $K_4Fe(CN)_6$ was added in excess, the proportion of Mn in the compound decreased. Wyrubow (*Annalen*, 1835, **8**, 444) suggested the formation of $K_2MnFe(CN)_6$ and also $Mn_2Fe(CN)_6$. Werner (*Z. anal. Chem.*, 1909, **58**, 23) obtained a white difficultly soluble compound $Mn_2Fe(CN)_6$. Britton and Dodd (*J. Chem. Soc.*, 1933, 1543) titrated metal salts with $K_4Fe(CN)_6$ conductometrically by means of a glass electrode and reported the formation of normal salt which was converted by further precipitant into $Mn_2Fe(CN)_6.x\,K_4Fe(CN)_6$ (where x is less than 1). The combination might be either physical or chemical. Williams (*Proc. Chem. Soc.*, 1913, **28**, 317) obtained $MnH_2Fe(CN)_6.4H_2O$ by treating manganese salts with $H_4Fe(CN)_6$. Eristavi and Barnabishvile (*J. Gen. Chem. USSR.*, 1936, **9**, 1880) reported the formation of a flocculent precipitate of $K_2MnFe(CN)_6$.

In view of the conflicting opinions and in the absence of any decisive views on the composition of this compound, it was considered worthwile to make its detailed study by physico-chemical investigations. The results provide more conclusive evidence on the composition of complex metallic ferro and ferricyanides (Saxena *et al.*, *Z. anorg. allgem. Chem.*, 1956, **285**, 90; 1954, **276**, 204; this *Journal*, 1954, **31**, 53, 157; 1952, **29**, 263, 284, 529, 535; 1951, **28**, 141, 221, 703). Whereas the composition of cobalt ferrocyanide and nickel ferrocyanide (Saxena, *Z. anal. Chem.*, 1957, **157**, 21; this *Journal*,

1957, **34**, 471) have already been studied, this paper incorporates the study on the composition of manganese ferrocyanide by potentiometric method.

Experimental

Merck's guaranteed extra pure reagents $MnCl_2$ and $K_4Fe(CN)_6$ were used. The strengths of the solutions were estimated by standard methods of analysis. Using different concentrations of the reactants, the titrations were performed both by the direct and the inverse methods *i.e.*, when $K_4Fe(CN)_6$ solution from the micro-burette was added to $MnCl_2$ solution in the electrode cell and *vice versa*. Potassium ferrocyanide solution containing 1% potassium ferricyanide was used to make the ferro-ferricyanide electrode (Kolthoff and Furman, "Potentiometric Titrations", New York, 1947, p. 323). A platinised platinum foil (*ibid.*, p. 204) was immersed in the solution of the titre and used as an indicator electrode in conjunction with a saturated calomel electrode. The electrode cell was kept in an electrically maintained thermostat to control temperature. E.M.F. was measured on a Cambridge p_H-meter. The titrations were also carried out in presence of alcohol up to a total concentration of 20%. The potential between the platinum indicator electrode and the reference half-cell has been measured and plotted against the volume of the titrant. A sharp deflection in the curve occurs at the end-point which is marked by a pronounced maxima in dE/dV (20 c.c. of the reagent was taken in the cell each time).

Table I

Summary of results of potentiometric titrations.

$K_4Fe(CN)_6$ solution (Molarity).	$MnCl_2$ solution (Molarity).	Points of equivalence. c.c. of $K_4Fe(CN)_6$ or $MnCl_2$ soln. required for the formation of $4Mn_2Fe(CN)_6.3K_4Fe(CN)_6$. Calc.	Obs. from dE/dV in presence of alcohol. 0%.	10%.	20%
		Direct titrations (Figs. 1-2)			
M/5	*M*/20	4.375	4.34	4.36	4.38
M/20	*M*/100	3.50	3.44	3.46	3.48
		Inverse titrations (Figs. 3-4)			
M/20	*M*/5	5.71	5.88	5.75	5.70
M/100	*M*/20	4.57	4.64	4.60	4.58

Discussion

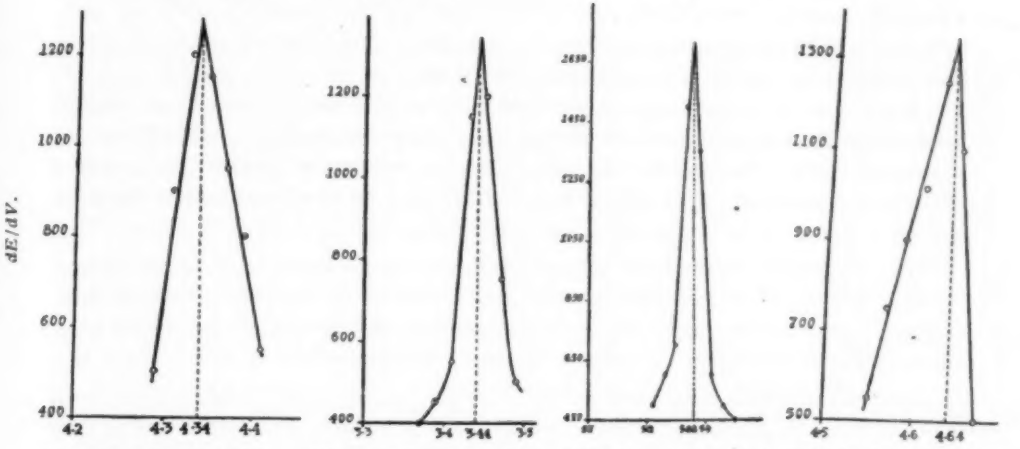
From the strengths of solution of $K_4Fe(CN)_6$ (*M*/5) and $MnCl_2$ (*M*/20), the calculated titre equivalents for the formation of more probable compounds are given below.

1. Titre value for 20 c.c. of *M*/20-$MnCl_2$ in direct titration	$K_2MnFe(CN)_6$. 5.0 c.c.	$Mn_2Fe(CN)_6$. 2.5 c.c.	$4Mn_2Fe(CN)_6.3K_4Fe(CN)_6$. 4.375 c.c.
		[*M*/5-$K_4Fe(CN_6)$ solution]	
2. Titre values for 20 c.c. of *M*/20-$K_4Fe(CN)_6$ in inverse titration	5.0 c.c.	10 c.c.	5.71 c.c.
		[*M*/5-$MnCl_2$ solution]	

The titre values required for the formation of above compounds employing different concentrations of reactants can be calculated accordingly, both in the case of the direct and the inverse titrations.

FIG. 1 FIG. 2 FIG. 3 FIG. 4

Direct titrations *Reverse titrations*



M/5-K_4FeCy_6 (c.c.) *added to* 20 c.c. *of* *M*/20-$MnCl_2$. | *M*/20-K_4FeCy_6 (c.c.) *added to* 20 c.c. *of* *M*/100-$MnCl_2$. | *M*/5-$MnCl_2$ (c.c.) *added to* *M*/20-$FeCy_6$ (20 c.c.). | *M*/20-$MnCl_2$ (c.c.) *added to* *M*/100-K_4FeCy_6 (20 c.c.)

It is clear from Figs. 1-4 that the reaction between $MnCl_2$ and $K_4Fe(CN)_6$ can be successfully followed potentiometrically, applying ferro-ferricyanide electrode with either of the reactants alternately used as the titre. The point of inflection, calculated from the maxima in dE/dV, occurs at a stage where the molecular ratio of the reactants, $K_4Fe(CN)_6$: $MnCl_2$ is as 7:8 and corresponds to the formation of the compound $4Mn_2Fe(CN)_6.3K_4Fe(CN)_6$ and is much different from those required for the formation of other probable compounds, $K_2MnFe(CN)_6$ and $Mn_2Fe(CN)_6$, as reported earlier in literature.

The titration curves have a regular shape ; a sharp jump in potential occurs at the equivalence point and the results are accurate and reproducible. The E. M. F. becomes constant rapidly after each addition of the reagent in aqueous as well as in alcoholic medium, and the whole titration takes little time. The addition of alcohol improves the results (Table I), but it does not have any appreciable effect on the nature of curves or on the magnitude of the potential break in either case.

According to the equation $Fe(CN)_6^{4-} \rightleftharpoons Fe(CN)_6^{3-} + \ominus$, the oxidation potential of the ferricyanide-ferrocyanide electrode is given by

$$E = E_0 + 0.059 \log Fe(CN)_6^{4-}/Fe(CN)_6^{3-} \text{ at } 25°.$$

In the titration of $MnCl_2$ with $K_4Fe(CN)_6$ solution containing a little ferricyanide, so long as there is an excess of Mn^{2+} ions in solution, the concentration of ferrocyanide is small, and so the potential of the electrode is high. As soon as manganese ions are

quantitatively precipitated, the next drop of ferrocyanide solution added causes an increase in $Fe(CN)_6^{4-}$ and, hence, a decrease in the oxidation potential occurs, indicating a sharp fall in direct titration curves at the end-point. Similarly, a marked upward jump in E. M. F. is observed at the equivalence point in the reverse titration curves due to the increase in the oxidation potential of the ferro-ferricyanide electrode.

It is to be noted that the titrations of $MnCl_2$ with $K_4Fe(CN)_6$ are accompanied by a marked change in colour at the equivalence point, *i.e.*, from greyish to white in direct titrations and from white to grey in reverse titrations. The change in colour is so sharp that the end-point can be accurately detected visually.

It is clear from Table I that the observed titre values in direct titrations are slightly lower than the calculated points of equivalence in aqueous medium ; while in the case of inverse titrations they are slightly higher. In the presence of increasing amounts of alcohol, the observed titre values, both in the case of direct and inverse titrations, gradually approach the calculated values more closely.

The discrepancy between the observed and the calculated titre values in aqueous medium and the subsequent change when the titrations are carried out in alcoholic medium, support our views on the hydrolytic and adsorptive behaviour of such ferro- and ferricyanide complexes (cf. Saxena, previous publications).

In direct titrations, adsorption of Mn^{2+} ions by the precipitate would tend to lower the titre values in aqueous medium. In the inverse titrations, manganese ferrocyanide on hydrolysis would release some $Fe(CN)_6$ ions which will consume some extra amount of $MnCl_2$, howsoever little it may be and, hence, the amount of $MnCl_2$ required will be slightly greater than the calculated equivalent. Alcohol suppresses adsorption and hydrolysis and decreases the solubility of manganese ferrocyanide, and hence, a closer approach to the theoretical values is envisaged by the experimental results. In presence of 20% alcohol, the observed values almost coincide with the calculated titre values.

The results of potentiometric titrations suggest that manganese ferrocyanide is not a pure compound but a double salt represented by a $4Mn_2Fe(CN)_6.3K_4Fe(CN)_6$ and are in confirmity with the observations of the author, obtained by applying other physico-chemical methods, such as conductometric and thermometric titrations (R.S. Saxena, *Proc. Indian Science Congress*, Part III, 1958, p. 93).

Quantitative work on adsorption and hydrolysis in the case of manganese ferrocyanide has been carried out and the results will be communicated shortly.

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FORMATION OF COMPOUNDS OF CUPROUS IODIDE WITH ALKALI AND ALKALINE EARTH METAL IODIDES IN ACETONE

By Sarju Prasad and Kailash Nath Upadhyaya

The double compounds of Cu^{I} iodide with alkali and alkaline earth metal iodides have been prepared in acetone and their general properties studied.

A large number of complex halides of copper are reported in literature, but according to Remy and Laves (*Ber.*, 1933, **66**, 571) no complex with more than four halogens is known. Mann, Purdie and Wells (*J. Chem. Soc.*, 1936, 1503) examined the co-ordination compounds of cuprous iodide with tertiary phosphines and arsines (prepared by shaking phosphine or arsine with an equimolecular quantity of CuI, dissolved in concentrated solution of KI) and concluded that the above derivatives were formed from potassium cuproiodide $K_3[CuI_4]$.

Harris (*J. Proc. Roy. Soc. N.S. Wales*, 1950, III-**16**, 841) studied the co-ordination compounds of copper formed by treating tetrammine or *bis*-ethylenediamine copper^{II} halide with appropriate cuprous halide and concluded that these were complex compounds and not physical mixtures. Dutta and Sen (*J. Amer. Chem. Soc.*, 1917, **39**, 750) prepared the 2-covalent series iodides $M[CuI_2]$ from a series of organic bases. Wells and Herbert (*Z. anorg. Chem.*, 1890, **10**, 157) obtained colorless crystals corresponding to $(NH_4I)_2.Cu_2I_2$ or $4NH_4Cl.Cu_2Cl_2$ and $NH_4Cl.3Cu_2Cl_2$ by cooling the mixtures of a solution of cuprous iodide and ammonium iodide or cuprous chloride and ammonium chloride in presence of HCl and copper wire. Kohn (*Monatsh.*, 1912, **33**, 912) prepared a double cuprous iodide with quinoline methiodide, $C_9H_7N.CH_3I.CuI$, by a direct method.

A general survey of literature shows that practically no work has been done on the formation of double iodides of copper (ous) and alkali and alkaline earth metal iodides in organic solvents. The present investigation was therefore undertaken with a view to studying the formation of these compounds in acetone.

Experimental

A concentrated solution of a soluble iodide was prepared in a conical flask and cuprous iodide was added to it in small quantities when it dissolved. The process was continued till a small quantity of it was left at the bottom. The mixture was constantly shaken at least for 4 hours, left overnight, and filtered. The filtrate was concentrated on a sand-bath when a crystalline substance was obtained. It was washed several times with acetone, dried in steam-oven and analysed.

Copper was estimated by iodometric method, iodine as AgI, K as perchlorate, Ba and Sr as sulphates, nitrogen by Kjeldahls' method and Ca by precipitating it as calcium oxalate and titrating it against $KMnO_4$. Mg was estimated as $Mg_2P_2O_7$. Lithium and sodium could not be estimated and were found by difference.

All the chemicals used were of B.D.H. or Merck's E.P. quality.

TABLE I

Compounds of cuprous iodide with alkali and alkaline earth metal iodides.

No.	Other iodides.	Colour of the compounds isolated.	% Copper. Found.	% Copper. Calc.	% Iodine. Found.	% Iodine. Calc.	% Other metals. Found.	% Other metals. Calc.	Probable formulae.
1	LiI	Brown	19.30	19.59	78.60	78.27	2.10	2.14	$Li[CuI_2]$
2	NaI	Light brown	18.73	18.68	74.38	74.56	6.84	6.76	$Na[CuI_2]$
3	KI	Brown	17.78	17.83	70.80	71.20	11.42	10.97	$K[CuI_2]$
4	NH_4I	Dirty brown	18.93	18.95	75.60	75.68	5.47	5.37	$NH_4[CuI_2]$
5	MgI_2	Dull white	19.73	19.29	76.45	77.02	3.82	3.69	$Mg[2CuI_2]$
6	CaI_2	Reddish brown	18.98	18.84	75.12	75.22	5.90	5.94	$Ca[2CuI_2]$
7	SrI_2	,,	17.56	17.58	70.22	70.29	12.22	12.13	$Sr[2CuI_2]$
8	BaI_2	Brown	16.35	16.46	66.23	65.76	17.42	17.78	$Ba[2CuI_2]$

Attempts were made to prepare the analogous compounds of CdI_2, Hg_2I_2 and FeI_2, but no compound could be isolated in these cases.

General Properties.—In all these cases slightly coloured and crystalline compounds, fairly stable, if kept out of contact with moist air, were obtained. These are hygroscopic and decompose when left in air for a long time. The compounds obtained with alkaline earth metal iodides are more stable than those obtained with alkali metal iodides, the ammonium compound being most stable. These are fairly soluble in acetone and ammonium hydroxide, sparingly so in alcohol and insoluble in water, benzene and pyridine. On treatment with dilute HNO_3 or HCl, these dissociate into their components, but dissolve in HNO_3 or HCl (conc.).

Cuprous iodide is insoluble in acetone, but its solubility increases in the presence of these iodides which indicates the formation of complex compounds. An examination of the table shows that one molecule of an alkali metal iodide combines with one molecule of cuprous iodide, but one molecule of alkaline earth metal iodide combines with two molecules of CuI ; the compounds formed may be represented as $M[CuI_2]$ and $M[2CuI_2]$. All these compounds are unstable and decompose when heated above 150° or boiled with water. This seems to be due to the fact that the E.A.N. of copper in these compounds is 32, and therefore these do not possess a stable configuration.

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DERIVATION OF AN EQUATION FOR SLOW COAGULATION OF COLLOIDS ON THE BASIS OF SMOLUCHOWSKI'S THEORY

By B. N. Ghosh

Assuming that ϵ in Smoluchowski equation,

$$\Sigma n = \frac{n_o}{1 + \frac{t}{T}\epsilon}$$

for slow coagulation, is equal to $K/(1 + at)$ (where K and a are constants and t, the time measured from the start of coagulation), an equation has been deduced which can be tested by direct counting of n_o and Σn in an ultramicroscope. The agreement between the observed values of Σn and those calculated from the equation is fair. With the same assumptions as above, combined with Rayleigh's equation for scattering of light by particles, an equation $D_t/D_i = (1 + bt)/(1 + at)$ has been deduced in which a and b are constants and D_i and D_t are the galvanometer deflections initially (*i.e.* at $t=0$) and after a time t respectively. The latter equation agrees satisfactorily with the experimental data.

It is generally accepted that in the region of rapid coagulation of colloids by electrolytes, the following equation of Smoluchowski holds good (Zsigmondy, *Z. physikal. Chem.*, 1917, **92**, 600; Westgren and Reitstotter, *ibid.*, p. 750).

$$\Sigma n = \frac{n_o}{1 + \frac{t}{T}} \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

where Σn represents the sum of single, double, triple etc. particles per unit volume of the system after a time, t, following the addition of an electrolyte to the colloid, n_o, the total number of particles initially present per unit volume, and T, a characteristic constant. For slow coagulation, this equation was found inadequate, and Smoluchowski therefore suggested a modified form of the above equation, expressed as:

$$\Sigma n = \frac{n_o}{1 + \frac{t}{T}\epsilon} \quad \ldots \quad \ldots \quad \ldots \quad (2)$$

where ϵ represents the percentage of successful encounter of the approaching particles with the central one. The experimental results of Kruyt and Van Arkel (*Kolloid Z.*, 1923, **32**, 29), Mukherjee and Mazumdar (*J. Chem. Soc.*, 1924, **125**, 785), Rai and Ghosh (*Kolloid Z.*, 1957, **154**, 146) and others in the region of slow coagulation do not agree, except at the initial stages of coagulation, with this modified equation also. It appears that in equation (2), ϵ decreases as t increases. In some cases of slow coagulation, Σn ceases to decrease any further after some time. This fact can be accounted for broadly by assuming that

$$\epsilon = \frac{K}{1 + at} \quad \ldots \quad \ldots \quad \ldots \quad (3)$$

where K and a are constants.

Substituting this value of ϵ in equation (2), we get the following expression after simplification :

$$\frac{\Sigma n}{n_o} = \frac{1 + at}{1 + \beta t} \quad \ldots \quad \ldots \quad \ldots \quad (4)$$

where a and β are constants and $\beta > a$.

Before proceeding further, it is necessary to examine whether the assumption made above, when introduced into the differential equation for the kinetics of coagulation, does lead to an expression of the same form as equation (2).

For rapid coagulation (vide Kruyt, "Colloid Science", 1952, Vol. I, p. 281) the differential equation can be written as :

$$\frac{d\sum_{k=1}^{\infty} n_k}{dt} = - 4\pi D_1 R \left(\sum_{k=1}^{\infty} n_k\right)^2 \quad \ldots \quad \ldots \quad (5)$$

where R represents the radius of the sphere of attraction and is approximately twice the radius of a primary particle, and D, the diffusion constant.

For slow coagulation, introduction into equation (5) of the Smoluchowski factor, ϵ, a constant, leads to the expression :

$$\frac{d\sum_{k=1}^{\infty} n_k}{dt} = - 4\pi D_1 R \epsilon \left(\sum_{k=1}^{\infty} n_k\right)^2. \quad \ldots \quad \ldots \quad (6)$$

Since the rate factor $4\pi D_1 R\epsilon$ decreases with time, it is assumed that ϵ alone is not constant but decreases with time. We may then write equation (6) as

$$\frac{d\sum_{k=1}^{\infty} n_k}{dt} = 4\pi D_1 R \frac{1}{a} \cdot \frac{d\epsilon}{dt} \left(\sum_{k=1}^{\infty} n_k\right)^2 \quad \ldots \quad \ldots \quad (7)$$

That is, in place of ϵ in equation (6), we write $d\epsilon/dt$ and introduce a constant "$1/a$" in equation (7) for necessary adjustment. The solution of the differential equation (7) leads to the expression :

$$\Sigma n_k = \frac{n_o}{1 + \frac{t}{T}\epsilon}$$

when ϵ is put equal to $K/(1+at)$, as stated already. Therefore the assumption, we have made, does not lead to any incompatibility.

How far equation (4) is in agreement with the experimental data has been discussed herein.

Experimental Data and their Interpretation

Ultramicroscopic counting of particles of several selenium sols at different intervals of time, both in the regions of slow and rapid coagulation, was made by Kruyt

* The negative sign disappears because ϵ decreases with time.

and Van Arkel (*loc. cit.*). A few of their data for slow coagulation are recorded in Table I in which Σn_{obs} represents the number of particles found by ultramicroscopic counting after a time, t, following the addition of electrolyte to the colloid, and Σn_{calc} represents the corresponding number calculated from equation (4). For the evaluation of a and β in equation (4), a curve is drawn by plotting the observed values of Σn against t and then from known values of Σn and t, for two points in the curve, a and β are evaluated.

TABLE I

Selenium sol 17 C.

KCl = 50 mM/litre. $n_0 = 29.7 \times 10^9$/c.c. Radius of particle = 52. $a = 0.022$. $\beta = 0.11$.

t (in hrs.)	0.66	4.25	19.0	43.0	73.0	167.0
$(\Sigma n_{obs}) \times 10^{-9}$	20.8	19.1	14.4	10.7	7.7	6.5
$(\Sigma n_{calc}) \times 10^{-9}$	28.0	20.4	13.7	10.1	8.5	7.2

KCl = 60 mM/litre. $n_0 = 29.7 \times 10^9$. $a = 0.3$. $\beta = 1.4$.

t (in hrs.)	0.25	0.83	1.5	19.5	49.5	144.0
$(\Sigma n_{obs}) \times 10^{-9}$	21.4	16.6	14.5	9.07	5.6	3.4
$(\Sigma n_{calc}) \times 10^{-9}$	23.4	17.2	13.9	7.2	6.7	6.5

Selenium sol 14A.

KCl = 30 mM/litre. $n_0 = 36.9 \times 10^9$. $a = 0.013$. $\beta = 0.04$. Radius = 62

t (in hrs.)	0.25	5.25	28.5	73.0	241.0	337.0
$(\Sigma n_{obs}) \times 10^{-9}$	35.0	33.3	22.3	13.82	14.3	13.9
$(\Sigma n_{calc}) \times 10^{-9}$	36.5	32.6	23.6	...	14.3	13.6

TABLE II

Arsenius sulphide sol.

$D_i = 124$. NaCl = $N/13$. $b = 0.006$. $a = 0.035$

t (in min.)	0	5	10	20	25	30	40
D_t obs	124	111	96.5	80	77	71	65.5
D_t calc	...	108.7	97.5	81.7	76.1	70.8	64.1

$D_i = 124$. NaCl = $N/11$. $b = 0.003$. $a = 0.2$.

t (in min.)	0	5	10	15.0	20.0	25.0	30.0	45.0	55.0	75.0
D_t obs	124	59	39	30.0	23.0	19.0	16.2	10.0	9.0	5.5
D_t calc	...	61	40	29.6	23.3	18.8	16.1	10.7	8.9	6.0

$D_i = 37$. $AlCl_3 = N/2{,}500$. $b = 0.2$. $a = 0.4$.

t (in min.)	0	2	4	6.8	16.4	26.8	37.3	53.0
D_t obs	37	28.5	25.6	23.8	21.3	20.5	20.0	19.0
D_t calc	...	28.7	25.6	23.5	21.0	20.1	19.7	19.3

In Table II are recorded the data taken from Fig. 1 and Fig. 3 of the paper of Mukherjee and Mazumdar (*loc. cit.*). In this table D_t represents the galvanometer deflection corresponding to the intensity I_t of the light transmitted through the glass cell of length L containing the colloid after a time, t, following the addition of electrolyte

to it and D_i, the deflection corresponding to intensity I_i of light transmitted through the colloid in the same cell at $t=0$, *i.e.*, in the absence of electrolyte. Let D_o represent the deflection corresponding to the intensity I_o of light transmitted through water in the aforesaid cell.

Now we can write

$$I_t = I_o - I_a - I_s \quad \ldots \quad \ldots \quad \ldots \quad (5)$$

where I_a and I_s represent the light absorbed and scattered by the colloidal particles in the cell. From the Beer-Lambert law, when absorption is small, and Rayleigh's theory, it follows that

$$I_a = I_o\ (KCL) \text{ and } I_s = I_o h n_o V_1^2 L$$

where K is the extinction coefficient, C, the concentration of the particles, h is a constant under the conditions of the experiment, V_1, the volume of a primary particle and n_o, their number in unit volume of the colloid. Assuming that KCL does not change during coagulation and I'_s, the altered value of I_s after a time, t, from the start of coagulation, we have

$$I_t = I_o\ (1 - KCL - hV_r^2 \Sigma nL) \quad \ldots \quad \ldots \quad (6)$$

where V_r represents the root mean square volume of a particle.

Similarly $$I_i = I_o\ (1 - KCL - LhV_1^2 n_o). \quad \ldots \quad \ldots \quad (7)$$

Substituting D_o, D_i, and D_t for I_o, I_i and I_t, respectively, we have from equations (6) and (7)

$$D_t = D_o\ (1 - KCL - LhV_r^2 \Sigma n)$$

and $$D_i = D_o\ (1 - KCL - LhV_1^2 n_o).$$

Hence $$D_i - D_t = D_o(LhV_r^2 \Sigma n - LhV_1^2 n_o). \quad \ldots \quad \ldots \quad (8)$$

Assuming that in the region of slow coagulation also, the distribution of particles in different size groups follows the same type of equation as that for rapid coagulation, deduced by Smoluchowski, it can be shown (vide Kruyt, "Colloid Science", 1952, Vol. I, pp. 297-298) that

$$V_r^2 \Sigma n = V_1^2 n_o\ (1 + \frac{2t}{T} \epsilon).$$

Substituting this value of $V_r^2 \Sigma n$ in equation (8) and putting γ for $2/T$, we have

$$D_i - D_t = D_o hL\ n_o V_1^2\ (1 + \epsilon\gamma t - 1)$$

or $$1 - \frac{D_t}{D_i} = \frac{D_o}{D_i}\ hLn_o V_1^2 \gamma \epsilon t. \quad \ldots \quad \ldots \quad (9)$$

Now substituting $K/(1 + at)$ for ϵ, as discussed previously, in equation (9), we have

$$\frac{D_t}{D_i} = 1 - \frac{K_1 t}{1 + at} \quad \ldots \quad \ldots \quad \ldots \quad (10)$$

where $K_1 = \frac{D_o}{D_i}\ hLn_o V_1^2 \gamma K$ and is a constant under the conditions of the experiments.

Equation (10) can also be put in the form :

$$\frac{D_t}{D_i} = \frac{1 + (a - K_1)t}{1 + at} = \frac{1 + bt}{1 + at} \quad \ldots \quad \ldots \quad (11)$$

where $b = (a - K_1)$ and is a constant. It is evident that b may have a positive or a negative value depending on the values of a and K_1.

In Table II $D_{t\,obs}$ represents the observed values and $D_{t\,calc}$, those calculated from equation (11) from the corresponding values of t and known values of D_i, and the values of b and a, found from two values of D_t observed and the corresponding values of t. It will be noticed that the agreement between the observed and the calculated values of D_t is quite good.

DISCUSSION

It will be noticed from the data recorded in Table I that the agreement between the observed values Σn and those calculated from equation (4) is fair except in one or two cases. An examination of the experimental data of Kruyt and Van Arkel (*loc. cit.*) will show that erratic value of the number of particles is sometimes obtained in ultramicroscopic counting. Thus for sol 17C containing 50 mM/litre of KCl at $t = 0.66$ hrs., $\Sigma n_{obs} = 20.9 \times 10^9$ may be one such erratic value. For the same sol containing 60mM/litre of KCl, the observed value of Σn at $t = 49.5$ hrs. is 5.6. Since the original sol contains 29.7×10^9 particles per c.c., it is obvious that the average aggregates consist of nearly 6 primary particles at this stage. Hence, there should then be many aggregates in the sol which should consist of more than 6 primary particles. As the radius of the primary particles is 5.2×10^{-6} cm, therefore these big aggregates of radius greater than 3×10^{-5} cm will begin to settle down and will net smaller particles in the process, leading to a lower value of Σn. Thus, from this stage onward, there is bound to be divergence between the observed and the calculated values of Σn.

It will appear from Table II that the values of D_t (observed) agree well with the corresponding values of D_t (calculated) from equation (11). It may, however, be mentioned that although equation (11) is of the same form as equation (4), and both are deduced from Smoluchowski's equation for slow coagulation on the assumption that $\epsilon = K/(1+at)$, yet they differ in one respect, namely, that the constant b in equation (11) may have a negative value. In fact, for the arsenious sulphide sol containing NaCl of strength $N/11$, b has actually a small negative value, -0.003. This difference between the equations (4) and (11) is to be attributed to the fact that they have been suitably adapted for test by different methods. It may therefore be concluded that equation (4) agrees fairly with the experimental data, while equation (11) does so satisfactorily.

Since the assumption, that in slow coagulation ϵ decreases with time, leads to useful deductions, attempt should be made to correlate it with some of the factors which change with progress of coagulation. The most obvious one is the average size of the particles. According to Verwey and Overbeek ("Theory of the Stability

of Lyophobic Colloids", 1948, p. 177) the stability of a sol in the presence of an electrolyte (uni-univalent), provided that its concentration is low, say about 27 mM/litre, should increase with the radius of the particles up to about 2×10^{-5}cm, after which it should decrease sharply. The experimental data recorded in Tables I and II, on the other hand, indicate that the rate factor of coagulation decreases with time even when the concentration of the added electrolyte is of the order of $N/15$. There is, thus, some difficulty in the way of correlating ε with the energy of repulsion between two interacting particles through their average radius. For the elucidation of the problem further quantitative work is obviously necessary.

In conclusion the author takes the opportunity of expressing his sincere thanks to Mr. K. C. Basak, Director, Economic Research Section, Indian Central Jute Committee, for his helpful criticism.

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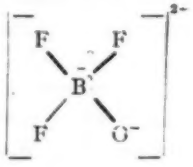
OXYFLUOBORATES AND THEIR CHEMICAL ANALOGY WITH THE SULPHATES. PART I. OXYFLUOBORATES OF ALKALI METALS, ALKALINE EARTH METALS AND LEAD

By Asimbikash Ray and Grihapati Mitra

The oxyfluoborates of lead, strontium and barium have been described. Oxyfluoborates of the alkali metals could not be prepared. The acid oxyfluoborate of potassium has, however, been prepared. Ammonium oxyfluoborate has been isolated with three molecules of BF_3. The salts of the alkaline earth metals are sparingly soluble in water. The powder pictures of lead oxyfluoborate and barium oxyfluoborate reveal isomorphism with the corresponding sulphates.

The fluoborate ion is well established, but no mention of BF_3O^{2-} ion is found in the literature. Both from chemical as well as structural points of view, BF_3O^{2-} ion promises some interest; it has therefore been thought desirable to study the chemistry of this ion. The present paper deals with the chemistry of the oxyfluoborate of the alkali and alkaline earth metals. The structure of this new oxyfluoborate ion, in keeping with the structures of BF_4^{2-} and BeF_4^{2-} ions, should be



It is needless to mention, however, that there should be other resonating structures. The ionic and atomic radii of oxygen and fluorine are very close to each other.

Element.	Atomic radius (Å).	Ionic radius (Å).
Fluorine	0.64 (F)	1.33 (F^-).
Oxygen	0.66 (O)	1.52 (O^{2-})

Thus, it becomes apparent that BF_3O^{2-} should resemble other ions like SO_4^{2-}, PO_3F^{2-}, BeF_4^{2-} etc., both in size as well as in properties. Present investigation has revealed that both barium and lead oxyfluoborates are isomorphous with the corresponding sulphates. The analogy between the oxyfluoborates and the corresponding sulphates, both in composition as well as in properties, has also been recognised.

Experimental

C. P. quality compounds were taken as starting materials. The compounds were decomposed by fusing with excess of alkali metal carbonate. The amount of fluoride ions present in the compounds was determined as calcium fluoride;

boron was quantitatively estimated as methyl borate and the other elements were determined by following the usual methods (Scott, "Standard Methods of Chemical Analysis", D. Van Nostrand Co. Inc., New York).

Oxyfluoboric Acid.—BF_3 at lower temperatures serves as the true anhydride of H_2BF_3O. Compounds such as $BF_3.H_2O$, $BF_3.2H_2O$ and $BF_3.3H_2O$ were described previously. In view of the fact that aqueous solutions of $BF_3O.H_2O$ and H_2SO_4 reveal close analogy in their equivalent conductivities (unpublished work), these compounds, so long considered as the hydrates of boron trifluoride, should better be represented as H_2BF_3O, $H_2BF_3O.H_2O$ and $H_2BF_3O.2H_2O$, in analogy with the corresponding hydrates of H_2SO_4.

Oxyfluoborates of the Alkali Metals.— The pure alkali metal oxyfluoborates could not be prepared. When equimolecular quantities of HF, H_3BO_3 and twice the molecular quantity of KF were used as the starting materials, the acid salt of the oxyfluoborate ion was obtained. The methods of preparation of the soluble oxyfluoborates have been described in detail in Part II of this series (this *issue*, p. 690).

$$2KF + H_3BO_3 + HF = KHBF_3O + KOH + H_2O$$

The compound obtained in this case was washed and dried in the usual way and then analysed. (Found: F, 45.39; K, 31.61; B, 8.62. Calc. for $KHBF_3O$: F, 45.97; K, 31.53; B, 8.73%).

The detailed description of the methods of preparation and also the results of analysis of other acid oxyfluoborates are not given here. These compounds have been reported previously in the name of the hydroxyfluoborates (Sowa *et al.*, *J. Amer. Chem. Soc.*, 1935, **57**, 454; Meerwein, *Ber.*, 1933, **66**, 411).

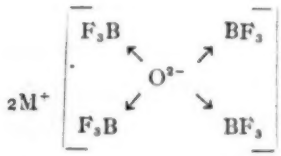
A solution of nitron acetate was added to a concentrated solution $KHBF_3O$. No precipitate was obtained. KBF_4, however, gave an instantaneous precipitation. This observation indicates that this potassium salt behaves more like $KHSO_4$ rather than KBF_4.

Attempts were made to isolate the ammonium salt by heating cautiously ammonium bifluoride with the requisite quantity of boric acid. It was thought that the absence of water molecules might prevent the hydrolysis:

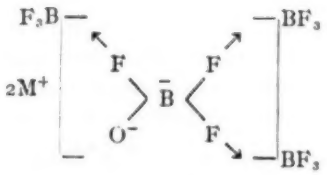
$$M_2BF_3O + H_2O = MHBF_3O + MOH.$$

In this case, however, a compound having the formula $(NH_4)_2BF_3O.3BF_3$ was obtained. [Found: F, 70.63; NH_3, 10.33; B, 13.09. Calc. for $(NH_4)_2\ BF_3O.3\ BF_3$: F, 70.51; NH_3, 10.51; B, 13.38%].

Several compounds of this type have been described previously in the name of fluoborates and so the detailed description of the work is not given here. These compounds had, however, been represented so long (Booth and Martin, "Boron Trifluoride and its Derivatives", John Wiley and Sons, New York; "Fluorine Chemistry", edited by J. Simons, Academic Press Inc., New York, p. 203)as:



It may be suggested that oxygen is too electronegative to play the part of the central element in a complex ion, and in fact, this is the only compound reported with oxygen at the centre. After the isolation of BF_3O^{2-} ion as a separate discrete individual, these compounds should better be represented as



Further work is, however, required to confirm this.

Strontium Oxyfluoborate.—A solution of strontium nitrate was cooled to 0° by keeping the beaker in a bath of ice and salt. To this solution was added a cold saturated solution of copper oxyfluoborate with constant stirring. A white insoluble powdery substance was obtained. It was filtered under gentle suction, washed several times with water and finally with alcohol. The compound was dried at 100° and analysed. (Found: F, 32.81; B, 6.26; Sr, 50.50. $SrBF_3O$ requires F, 33.24; B, 6.31; Sr, 51.20%).

Strontium oxyfluoborate is a finely divided crystalline solid which is sparingly soluble in water and can be heated to a high temperature without decomposition.

Barium Oxyfluoborate.—The solutions of the soluble oxyfluoborates (Part II, *loc. cit.*) have been found to be slightly acidic. A covalently bound oxygen atom is never dissociated in preference to the fluorine atom from any complex fluoride anion. The dissociation in solution may be represented as:

$$BF_3O^{2-} + H_2O = BO(OH)F_2^{2-} + H^+ + F^-.$$

Due to presence of this free fluoride ion the calcium oxyfluoborate could not be isolated. Barium oxyfluoborate was isolated by suppressing the secondary dissociation by the addition of a few drops of amyl alcohol, otherwise the method of procedure was same as described under strontium oxyfluoborate. (Found: F, 25.40; B, 4.40; Ba, 61.82. $BaBF_3O$ requires F, 25.77; B, 4.44; Ba, 62.10%).

As both barium fluoride and barium oxyfluoborate are insoluble in water, the exact nature of this white powder has been verified by X' ray analysis. The powder picture of this compound showed no line for BaF_2. The spacings calculated from the powder picture of $BaBF_3O$ are shown in Table I

TABLE I

d.	Intensity.	*d.*	Intensity.	*d.*	Intensity.
4.23	W	2.67	M	1.52	M
3.77	W	2.19	M	1.41	M
3.36	M	2.08	VS	1.33	M
3.24	M	1.65	M	1.31	W
3.01	S	1.58	W	1.28	W

VS = very strong. S = strong. M = Medium strong. W = weak.

On comparing this result with the standard spacings of $BaSO_4$, barium oxyfluoborate and barium sulphate are found isomorphous.

Lead oxyfluoborate was prepared by the double decomposition of the saturated solutions of lead nitrate and zinc oxyfluoborate. The heavy white precipitate formed was washed and dried by the methods described before. (Found: F, 19.34, 19.41; Pb, 71.01, 69.98. $PbBF_4O$ requires F, 19.58; Pb, 71.20%).

This compound was precipitated in a very finely divided form. Only the more intense lines obtained from the powder picture of this compound are shown below.

TABLE II

d.	Intensity.	*d.*	Intensity.
4.20	S	2.04	VS
3.29	S	1.98	M
3.20	M	1.69	W
2.98	VS	1.60	W

These compounds are found to be isomorphous with sulphate on comparing their powder pictures with the standard spacings of the latter.

The authors' best thanks are due to Prof. N. N. Ray, D.Sc., and Prof. P. C. Rakshit, Ph.D, both of the Presidency College, Calcutta, for giving all laboratory facilities during progress of the investigation.

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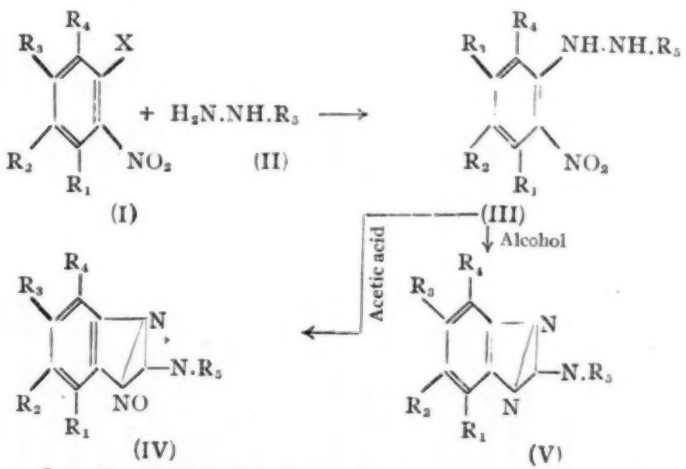
BEHAVIOUR OF CHLORONITROBENZENES WITH HYDRAZINE AND HYDRAZINE DERIVATIVES. PART VI. SOME 2-*p*-TOLYLNITRO-1 : 2 : 3-BENZOTRIAZOLES AND THEIR 1-OXIDES

By Shiam Sunder Joshi and Satya Prakash Gupta

A few phenyl-1 : 2 : 3-benzotriazoles and their 1-oxides have been obtained by condensation of halogeno-nitrobenzenes and *p*-tolylhydrazine. Where formation of more than one product was possible, only one triazole derivative could be isolated. Structure to these compounds has also been assigned.

A simple method for the synthesis of 2-aryl-1 : 2 : 3-benzotriazoles (Witt *Ber.*, 1912, **45**, 2381) or the corresponding -1-*N*-oxides (Gandmougin, *J. prakt. Chem*, 1907, *ii*, **76**, 134 ; *Ber.*, 1903, **36**, 3822) is by the condensation of phenylhydrazines with reactive halogen compounds having a nitro group in their *ortho* position (Willgerodt and Ferko, *J. prakt. Chem.*, 1888, *ii*, **37**, 351). The first product of the reaction is a hydrazobenzene derivative (III) (Fischer, *Annalen*, 1878, **190**, 132 ; Willgerodt *et al.*, *Ber.*, 1891, **24**, 1661 ; Werner *et al.*, *Ber.*, 1899, **32**, 3266) which in boiling acetic acid solution cyclises to a 2-phenyl-1 : 2 : 3-benzotriazole-1-oxide (IV) (Willgerodt, *J. prakt. Chem.*, 1889, *ii*, **40**, 253 ; Willgerodt and Ferko, *loc. cit.* ; Giua, *Gazzetta*, 1918, **48**, II, 13) and in alcoholic solution the 1-oxide (IV) first formed is reduced to a 2-phenyl-1 : 2 : 3-benzotriazole (V) (Willgerodt and Ferko, *loc. cit.* ; Walter, Dissertation, Freiburg, iB, 1889, S. 11 ; Sane and Joshi, this *Journal*, 1933, **10**, 459).



[X=Cl ; R_1=H ; R_2=NO_2 ; R_3=H ; R_4=H ; R_5=Ph]

During the present work, the behaviour of *p*-tolylhydrazine with a few reactive halogen compounds has been studied and as a result the preparation of some new 2-*p*-tolylnitro-1 : 2 : 3-benzotriazoles and their 1-oxides has been effected (Tables I and II).

TABLE I

2-p-*Tolyl*-1: 2 : 3-*benzotriazoles*.

Halogeno-nitrobenzene.	2-*p*-Tolyl-benzotriazole.	Yield.	M. P.	Colour.	Formula.	Found.	Calc.
1-Chloro-2 :4-dinitro-	6-Nitro-	85%	167°	Yellow needles	$C_{13}H_{10}O_2N_4$	N : 21.87%	22.05%
						C : 60.97	61.42
1-Chloro-2 :6-dinitro-	4-Nitro-	76	152°	Sepia needles	$C_{13}H_{10}O_2N_4$	N : 21.67	22.05
1-Chloro-2 :4 :6-trinitro-	4 :6-Dinitro-	80	182°	Dark sepia	$C_{13}H_9O_4N_5$	N : 23.09	23.41
1 :2-Dichloro-4 :6-dinitro-	4-Chloro-6-nitro	65	160°	Buff yellow	$C_{13}H_9O_2N_4Cl$	Cl : 12.10	12.30
						C : 53.62	54.07
1 :3-Dichloro-4 :6-dinitro-	5-Chloro-6-nitro-	85	199-201°	Dirty yellow	$C_{13}H_9O_2N_4Cl$	Cl : 11.98	12.30
1 :4-Dichloro-2 :6-dinitro-	6-Chloro-4-nitro-	74	207°	Light brown	$C_{13}H_9O_2N_4Cl$	Cl : 11.04	12.30
1-Chloro-2 :6-dinitro-4-methyl-	4-Nitro-6-methyl-	80	235°	Do	$C_{14}H_{12}O_2N_4$	N : 20.62	20.90
1-Chloro-4 :6-dinitro-3-methyl-	6-Nitro-5-methyl-	75	172°	Light yellow	,,	N : 20.67	20.90
						C : 62.55	62.69
1-Chloro-2 :4 :6-trinitro-3-methyl-	4 :6-Dinitro-7-methyl-	78	167°	Light brown	$C_{14}H_{11}O_4N_5$	N : 22.04	22 36
1 :2-Dichloro-4 :6-dinitro-5-methyl-	4-Chloro-6-nitro-7-methyl-	65	230°	Do	$C_{14}H_{11}O_2N_4Cl$	Cl : 11.54	11.74
2-Chloro-1-bromo-4 :6-dinitro-5-methyl-	4-Chloro-5-nitro-7-methyl-	70	230°	Do	,,	Cl : 11.43	11.74
1 :2-Dibromo-4 :6-dinitro-5-methyl-	4-bromo-6-nitro-7-methyl-	65	225°	Sepia prisms	$C_{14}H_{11}O_2N_4Br$	Br : 22.87	23.06
1-Chloro-2-bromo-4 :6-dinitro-5-methyl-	4-Bromo-6-nitro-7-methyl-	60	225°	Do	,,	Br : 22.78	23.06
1 :4-Dichloro-2 :6-dinitro-5-methyl-	6-Chloro-4-nitro-7-methyl-	72	210°	Sepia leaflets	$C_{14}H_{11}O_2N_4Cl$	Cl : 11.53	11.74
4-Chloro-1-bromo-2 :6-dinitro-5-methyl-	,,	80	210°	Do	,,	Cl : 11.59	11 74
1 :4-Dibromo-2 :6-dinitro-5-methyl-	6-Bromo-4-nitro-7-methyl-	65	182°	Dull yellow	$C_{14}H_{11}O_2N_4Br$	Br : 22.75	23.06
1-Chloro-4-bromo-2 :6-dinitro-5-methyl-	,,	60	182°	Do	,,	Br : 22.86	23.06
1 :2 :3-Trichloro-4 :6-dinitro-	4 :5-Dichloro-6-nitro-	85	192°	Light yellow	$C_{13}H_6O_2N_4Cl_2$	Cl : 21.79	21.98
1 :2 :3-Tribromo-4 :6-dinitro-	4 :5-Dibromo-6-nitro-	80	300° (d)	Light brown	$C_{13}H_6O_2N_4Br_2$	Br : 38.67	38.84
1 :2 :5-Trichloro-4 :6-dinitro-	4 :7-Dichloro-6-nitro-	76	165°	Tan	$C_{13}H_6O_2N_4Cl_2$	Cl : 21.67	21.98
1-Bromo-2 :5-dichloro-4 :6-dinitro-	4 :7-Dichloro-6-nitro	75	165°	Tan	$C_{13}H_6O_2N_4Cl_2$	Cl : 21.63	21.98
1 :2 :5-Tribromo-4 :6-dinitro-	4 :7-Dibromo-6-nitro-	65	222°	Faun leaflets	$C_{13}H_6O_2N_4Br_2$	Br : 38.47	38.84
1-Chloro-2 :5-dibromo-4 :6-dinitro-	4 :7-Dibromo-6-nitro-	72	222°	Do	,,	Br : 38.53	38.84
1 :3-Dichloro-2-bromo-4 :6-dinitro-	5-Chloro-4-bromo-6-nitro-	82	179°	Dark sepia	$C_{13}H_6O_2N_4ClBr$	Cl & Br : 22.89	31.43
1 :3-Dibromo-4 :6-dinitro-5-methyl-	5-Bromo-6-nitro-7-methyl-	74	>330°	Do	$C_{14}H_{11}O_2N_4Br$	Br : 22.89	23.06
1 :3-Dibromo-2 :4 :6-trinitro-5-methyl-	5-Bromo-4 :6-dinitro-7-methyl-	80	295° (d)	Buff	$C_{14}H_{10}O_4N_5Br$	Br : 20.30	20.41

d = decomposition

Table II

2-p-*Tolyl*-1 : 2 : 3-*benzotriazoles*-1-*oxides*.

Halogeno-nitrobenzene.	2-*p*-Tolyl-benzotriazole-1-oxide.	Yield.	M.P.	Colour.	Formula.	Found.	Calc.
1 Chloro-2 :4-dinitro-	6-Nitro-	70%	170°	Yellow needles	$C_{13}H_{10}O_3N_4$	N : 20.58	20.74
1-Chloro-2 :6-dinitro-	4-Nitro-	65	155°	Yellow	$C_{13}H_{10}O_3N_4$	N : 20.58	20.74
1 :2-Dichloro-4 :6-dinitro-	4-Chloro-6-nitro-	60	192°	Buff	$C_{13}H_9O_3N_4Cl$	Cl : 11.62	11.66
1 :3-Dichloro-4 :6-dinitro-	5-Chloro-6-nitro-	78	196°	Dirty yellow	$C_{13}H_9O_3N_4Cl$	Cl : 11.48	11.66
1 :4-Dichloro-2 :6-dinitro-	6-Chloro-4-nitro-	65	211°	Dark sepia	$C_{13}H_9O_3N_4Cl$	Cl : 11.53	11.66
1-Chloro-4 :6-dinitro-3-methyl-	6-Nitro-5-methyl-	68	194°	Light yellow	$C_{14}H_{12}O_3N_4$	N : 19.70	19.72
1-Chloro-2 :6-dinitro-4-methyl-	4-Nitro-6-methyl-	65	232°	Sepia	$C_{14}H_{12}O_3N_4$	N : 19.67	19.72
1-Chloro-2 :4 :6-trinitro-3-methyl-	4 :6-Dinitro-7-methyl-	70	205°	Dark sepia	$C_{14}H_{11}O_5N_5$	N : 21.09	21.28
1 :2 :3-Trichloro-4 :6-dinitro-	4 :5-Dichloro-6-nitro-	75	190°	Light yellow	$C_{13}H_8O_3N_4Cl_2$	Cl : 20.79	20.94
1 :2 :3-Tribromo-4 :6-dinitro-	4 :5-Dibromo-6-nitro-	70	270°	Sepia	$C_{13}H_8O_3N_4Br_2$	Br : 37.06	37.38
1 :2 :5-Trichloro-4 :6-dinitro-	4 :7-Dichloro-6-nitro-	60	245°	Dark sepia	$C_{13}H_8O_3N_4Cl_2$	Cl : 20.73	20.94
1-Bromo-2 :5-dichloro-4 :6-dinitro-	4 :7-Dichloro-6-nitro-	65	245°	Do	$C_{13}H_8O_3N_4Cl_2$	Cl : 20.65	20.94

Of the reactive halogen compounds investigated, 1-chloro-2 : 4 : 6-trinitro, 1 : 2-dichloro-4 : 6-dinitro-5-methyl-, 2-chloro-1-bromo-4 : 6-dinitro-5-methyl-, 1-chloro-2-bromo-4 : 6-dinitro-5-methyl-, 1 : 2-dibromo-4 : 6-dinitro-5 methyl-, 1:4-dichloro-2 : 6-dinitro-5-methyl-, 4-chloro-1-bromo-2 : 6-dinitro-5-methyl-, 1-chloro-4-bromo-2 : 6 dinitro-5-methyl-, 1 : 4-dibromo-2 : 6-dinitro-5-methyl-, 1:2 : 5-tribromo-4 : 6-dinitro-, 1-chloro-2 : 5-dibromo-4 : 6-dinitro-, 1 : 3-dichloro-2-bromo-4 : 6-dinitro-, 1 : 3-dibromo-4 : 6-dinitro-5-methyl- and 1 : 3-dibromo 2 : 4 : 6-trinitro-5-methyl-benzenes fail to furnish the corresponding 2-*p*-tolyl-1 : 2 : 3-benzotriazole-1-oxides.

Compounds that have only one nitro group in the *ortho* position to the reactive halogen atom can cyclise in one way when heated with *p*-tolylhydrazine, but when there are two nitro groups in both the *ortho* positions and the benzene ring is not symmetrically substituted, two products can be expected, according as the cyclisation takes place by interaction with one or the other of the two nitro groups. But it is noteworthy that in all such cases studied, only one compound could be isolated from the reaction product.

Structure to such compounds has been assigned on the basis of the known behaviour of reactive halogen compounds. Thus, the triazole, obtained by condensing *p*-tolylhydrazine with 1 : 4-dichloro-2 : 6-dinitro-5-methylbenzene (I : X = Cl ; R_1 = H ; R_2 = Cl ; R_3 = Me ; R_4 = NO_2), may be either 2-*p*-tolyl-6-chloro-4-nitro-5-methyl- (V : R_1 = NO_2 ; R_2 = Me ; R_3 = Cl ; R_4 = H ; R_5 = *p*-Tol) or 2-*p*-tolyl-6-chloro-4-nitro-7-methyl-1 : 2 : 3-benzotriazole (V : R_1 = NO_2 ; R_2 = H ; R_3 = Cl ; R_4 = Me ; R_5 = *p*-Tol). When the nitro group present in it is reduced and substituted by a chlorine atom by diazotisation and Gattermann's reaction, a dichloro-2-*p*-tolyl-benzotriazole is obtained. It was found to be identical by finding mixed melting point with 2-*p*-tolyl-4 : 6-dichloro-7-methyl-1 : 2 : 3-benzotriazole (V : R_1 = R_3 = Cl ; R_2 = H ; R_4 = Me ; R_5 = *p*-Tol) formed by a similar series of reactions from 2-*p*-tolyl-4-chloro-6-nitro-7-methyl-1:2:3-benzotriazole (V: R_1 = Cl ; R_2 = H ; R_3 = NO_2 ; R_4 = Me ; R_5 = *p*-Tol), a condensation product of 1 : 2-dichloro-4 : 6-dinitro-5-methylbenzene (I : X = R_4 = Cl ; R_1 = Me ; R_2 = NO_2 ; R_3 = H) and *p*-tolylhydrazine.

This is in agreement with the formation of 1-hydroxy-1 : 2 : 3-benzotriazoles (Joshi and Deorha, this *Journal*, 1952, **29**, 545) from substituted phenylhydrazines, where also the nitro group in *ortho* position to the methyl group is involved in the ring formation. Thus reactive halogen compounds: 1-chloro-2 : 4 : 6-trinitro-3-methyl-, 4-chloro-1-bromo-2 : 6-dinitro-5-methyl-, 1 : 4-dibromo-2 : 6-dinitro-5-methyl- or 1-chloro-4-bromo-2 : 6-dinitro-5-methyl-, 1 : 3-dibromo-4 : 6-dinitro-5-methyl-, and 1 : 3-dibromo-2 : 4 : 6-trinitro-5-methyl-benzenes give 4 : 6-dinitro-7-methyl-, 6-chloro-4-nitro-7-methyl-, 6-bromo-4-nitro-7-methyl-, 5-bromo-6-nitro-7-methyl- and 5-bromo-4 : 6-dinitro-5-methyl-2-*p*-tolyl-1 : 2 : 3-benzotriazoles respectively.

By the condensation of 1 : 2 : 5-trichloro-4:6-dinitrobenzene (I : X = R_1 = R_4 = Cl ; R_2 = NO_2 ; R_3 = H) with *p*-tolylhydrazine, three isomeric compounds, 2-*p*-tolyl-6 : 7-dichloro-4-nitro- (Va : R_1 = NO_2 ; R_2 = H ; R_3 = R_4 = Cl ; R_5 = *p*-Tol), 2-*p*-tolyl-4 : 7-dichloro-6-nitro- (Vb : R_1 = R_4 = Cl ; R_2 = H ; R_3 = NO_2 ; R_5 = *p*-Tol) and 2 *p*-tolyl-5 : 6

dichloro-4-nitro-1 : 2 : 3-benzotriazoles (Vc : $R_1=NO_2$; $R_2=R_3=Cl$; $R_4=H$; $R_5=p$-Tol) could possibly result ; but only one compound could, however, be isolated (Walter, Dissertation, Freiburg, iB, 1889, 3, 28). Identical compound, as found by the determination of the mixed melting point, is obtained by heating *p*-tolylhydrazine with 2 : 5-dichloro-1-bromo-4 : 6-dinitrobenzene (I : X=Br ; $R_1=R_4=Cl$; $R_2=NO_2$; $R_3=H$) in alcoholic solution. Both of them must therefore be 4 : 7-dichloro-6-nitro-2-*p*-toiyl-1 : 2 : 3-benzotriazole (Vb).

Similarly, 1 : 2 : 5-tribromo-4 : 6-dinitrobenzene (I : X=$R_1=R_4$ =Br ; $R_2=NO_2$; $R_3=H$) with *p*-tolylhydrazine gives 4 : 7-dibromo-6-nitro-2-*p*-tolyl-1 : 2 : 3-benzotriazole (V : $R_1=R_4=Br$; $R_2=H$; $R_3=NO_2$; $R_5=p$-Tol) which is identical with the product obtained from 1-chloro-2 : 5-dibromo-4 : 6-dinitrobenzene (I : X=Cl ; $R_1=R_4=Br$; $R_2=NO_2$; $R_3=H$).

Experimental

2-p-*Tolyl*-1:2:3-*benzotriazoles* were prepared by the action of *p*-tolylhydrazine on aromatic reactive halogen compounds (Method I) and also by the reduction of 2-*p*-tolyl-1: 2 : 3-benzotriazole-1-oxides (Method II).

Method I.—A mixture of halogeno-nitrobenzene, *p*-tolylhydrazine hydrochloride and sodium acetate (1 : 2 : 2) in alcohol was heated on a water-bath. Soon after shining crystals began to separate. After about half an hour the liquid was cooled and filtered. The compounds separating were crystallised from toluene.

Method II.—2-*p*-Tolyl-1 : 2 : 3-benzotriazole-1-oxides were refluxed for about 2 hours either with alcohol or better with alcohol containing hydrazine hydrate. The product was cooled, filtered and the solids separating were crystallised from toluene. Identical derivatives, as found by their mixed melting points, have been obtained by both the methods and described in Table I.

2-p-*Tolyl*-1 : 2 : 3-*benzotriazole*-1-*oxides* were prepared by heating an acetic acid solution of the reactive halogen compounds and *p*-tolylhydrazine (1 : 2) on a water-bath for about half an hour. The mass was cooled and filtered. The solid so obtained was crystallised from toluene. These have been described in Table II.

4-*Chloro*-6-*amino*-7-*methyl*-2-p-*tolyl*-1 : 2 : 3-*benzotriazole*.—4-Chloro-6-nitro-7-methyl-2-*p*-tolyl-1 : 2 : 3-benzotriazole was dissolved in a boiling mixture of equal quantities of alcohol and concentrated hydrochloric acid and then treated with an excess of zinc, added in small portions at a time. Boiling was continued till the liquid lost its colour. The mixture was filtered and alcohol evaporated off. An excess of sodium hydroxide solution was then added and the basic compound, set free, was extracted with benzene. On removing benzene and crystallising the residue from alcohol, light yellow crystals of 4-chloro-6-amino-7-methyl-2-*p*-tolyl-1 : 2 : 3-benzotriazole were obtained, m. p. 237°. (Found : Cl, 12.76. $C_{14}H_{13}N_4Cl$ requires Cl, 13.03%).

6-*Chloro*-4-*amino*-7-*methyl*-2-p-*tolyl*-1 : 2 : 3-*benzotriazole*.—6-Chloro-4-nitro-7-methyl-2-*p*-tolyl-1 : 2 : 3-benzotriazole on reduction by the method described above, gave 6-chloro-4-amino-7-methyl-2-*p*-tolyl-1 : 2 : 3-benzotriazole, cream in colour, m.p. 247°. (Found : Cl, 12.63. $C_{14}H_{13}N_4Cl$ requires Cl, 13.03%).

4 : 6-*Dichloro-7-methyl*-2-p-*tolyl*-1 : 2 : 3-*benzotriazole*.—4-Chloro-6-amino-7-methyl-2-*p*-tolyl-1 : 2 : 3-benzotriazole (2 g.) was dissolved in 40% acetic acid (25 c.c.), and HCl (conc., 8 c.c.) was added. The mixture was cooled (0°) and diazotised with a solution of sodium nitrite (2 g.) in water (12 c.c.) and filtered. The filtrate was treated with reduced copper (0.2 g.) and left overnight. The solid separating on crystallisation from benzene gave colorless crystals (1.4 g.), m.p. 167°. (Found : Cl, 23.80. $C_{14}H_{11}N_3Cl_2$ requires Cl, 24.31%).

Similarly, 6-chloro-4-amino-7-methyl-2-*p*-tolyl-1 : 2 : 3-benzotriazole on diazotisation and on application of Gattermann's reaction gave a colorless product, m.p. 167°, which was found to be identical with 4 : 6-dichloro-7-methyl-1 : 2 : 3-benzotriazole by mixed m.p.

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BARBITURATES. PART II. 5-METHYL-5-SUBSTITUTED BENZYL BARBITURATES AND THIOBARBITURATES

By J. P. Trivedi and J. J. Trivedi

Several 5-methyl-5-substituted benzyl barbiturates and thiobarbiturates as well as the substituted benzyl malonic esters required for the synthesis of above compounds have been prepared and described.

In continuation of our previous work (this *issue*, p. 661), barbiturates containing substituted benzyl group on C_5 have been synthesised and described in the present communication.

A few 5-alkyl-5-benzyl barbiturates were synthesised by John and Hill (*Amer. Chem J.*, 1911, **46**, 544) and Dox and Yoder (*J. Amer. Chem. Soc.*, 1922, **44**, 1141). 5-Ethyl-5-benzyl barbiturate was found to show convulsive properties. It has been observed that when the sum of C atoms in the groups at position-5 is larger than seven or eight, the hypnotic activity decreases and sometimes it leads to convulsions. The convulsive properties of 5-ethyl-5-benzyl barbiturate may perhaps be due to the sum of C atoms at position-5 exceeding eight C atoms. In the present work, barbiturates containing substituted benzyl and methyl groups on the C_5 atom have been prepared (sum total of C, not counting the nuclear substituents, is kept eight). The barbiturates were synthesised by the condensation of the appropriate methyl-substituted benzyl malonic ester with urea or thiourea.

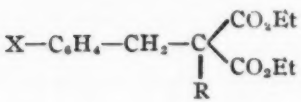
Experimental

Substituted malonates were prepared by first benzylating and then methylating the ethylmalonic ester (Leuchs, *Ber.*, 1911, **44**, 1509). The hitherto-unknown malonates are described in Table I.

Condensation of substituted malonates (0.1 *M*) with urea or thiourea (0.2 *M*) in presence of sodium ethylate (0.3 g. atom Na in 80 c.c. ethanol) was carried out as described in Part I (*loc. cit.*). The compounds are shown in Tables II and III with 25 to 30% yield

TABLE I

Substituted benzyl malonic esters.

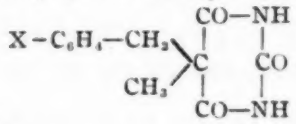


Compound. X=	R=	B. P.	Ref. Index	Formula	Found.	Calc.
o-Cl	H	140-48°/12 mm.	1.4880	$C_{14}H_{17}O_4Cl$	Cl : 12.4	12.5
p-Cl	H	188-90°/16	1 4975	,,	,,	,,
o-Br	H	180°/12	1.4940	$C_{14}H_{17}O_4Br$	Br : 24.2	24.3
m-Br	H	173-80°/7	1.5289*	,,	24.3	,,
p-Br	H	185-86°/10	1.5090	,,	,,	,,
o-CH_3	H	168-70°/10	1.4920	$C_{15}H_{20}O_4$	C : 68.0	68.2
					H : 7.5	7.6
m-CH_3	H	180°/30	1.5052	,,	C : 68.1	
					H : 7.5	
p-CH_3	H	208°/20	1.5049	,,	C : 68.1	
					H : 7.5	
2 CH_3(3 :4)	H	200°/60	1 4809*	$C_{16}H_{22}O_4$	C : 69 0	69 1
					H : 7.9	7.9
2 CH_3(2 :4)	H	180-85°/20	1.4932	,,	C : 69.0	69.1
					H : 7 8	7.9
2 CH_3(2 :5)	H	174-76°/12	1.4890	,,	C : 69.0	69.1
					H : 7.9	7.9
o-OCH_3	H	194°/13	1.4950*	$C_{15}H_{20}O_5$	C : 64.2	64.3
					H : 7.1	7.1
p-OCH_3	H	202°/25	1.4946	,,	C : 64.1	64.3
					H : 7.1	7.1
o-Cl	Me	140°/9	1.4960	$C_{15}H_{19}O_4Cl$	Cl : 11 8	11.9
p-Cl	,,	195°/16	1.4918	,,	Cl : 11 9	11.9
o-Br	,,	196°/15	1.5120	$C_{15}H_{19}O_4Br$	Br : 32.9	32.9
m-Br	,,	198-200°/7	1.5327*	,,	,,	,,
p-Br	,,	196°/11	1.5062	,,	,,	,,
o-CH_3	,,	182°/9	1.4812	$C_{16}H_{22}O_4$	C : 69.0	69.1
					H : 7 9	7 9
m-CH_3	,,	180°/10	1.5420*	,,	,,	,,
p-CH_3	,,	220°/20	1.5328*	,,	,,	,,
2 CH_3(3 :4)	,,	222°/50	1.4932	$C_{17}H_{24}O_4$	C : 69.8	69.9
					H : 8.2	8.2
2 CH_3(2 :4)	,,	206-208°/32	1.5108*	,,	,,	,,
2 CH_3(2 :5)	,,	182°/10	1.4880	,,	,,	,,
o-OCH_3	,,	196°/15	1 4918*	$C_{16}H_{22}O_5$	C : 65.3	65.3
					H : 7.4	7.5
p-OCH_3	,,	220°/25	1.5132*	,,	C : 65.2	65.3
					H : 7.4	7.5

Refractive indices were found at 25°; those marked with an asterisk were found at 38.5°.

TABLE II

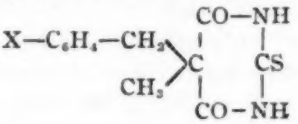
5-Methyl-5-(substituted benzyl)-barbituric acids.



Compounds X=	M. P.	Formula.	% Nitrogen Found.	Calc.
o-Cl	170°	$C_{12}H_{11}O_3N_2Cl$	10.4	10.5
p-Cl	197°	,,	10.5	,,
o-Br	151-52°	$C_{12}H_{11}O_3N_2Br$	9.0	9.0
m-Br	159-60°	,,	8.9	,,
p-Br	2·4°	,,	9.0	,,
o-CH_3	134°	$C_{13}H_{14}O_3N_2$	11.3	11.4
m-CH_3	127-28°	,,	,,	,,
p-CH_3	Wax-like	...	...	...
2 CH_3(3:4)	175°	$C_{14}H_{16}O_3N_2$	10.7	10.8
2 CH_3(2:4)	118°	,,	,,	,,
2 CH_3(2:5)	78°	,,	,,	,,
o-OCH_3	168°	$C_{13}H_{14}O_4N_2$	10.6	10.7
p-OCH_3	252°	,,	,,	,,

TABLE III

5-Methyl-5-(substituted benzyl)-2-thiobarbituric acids.



Compound. X=	M. P.	Formula.	% Nitrogen. Found.	Calc.
o-Cl	112°	$C_{12}H_{11}O_2N_2ClS$	9.9	9.9
p-Cl	220°	,,	,,	,,
o-Br	109-10°	$C_{12}H_{11}O_2N_2BrS$	8.5	8.6
m-Br	115°	,,	,,	,,
p-Br	131-32°	,,	,,	,,
o-CH_3	116°	$C_{13}H_{14}O_2N_2S$	10.6	10.7
m-CH_3	115°	,,	,,	,,
p-CH_3	114°	,,	10.5	10.7
2 CH_3(3:4)	100°	$C_{14}H_{16}O_2N_2S$	10.0	10.1
2 CH_3(2:4)	120°	,,	10.1	,,
2 CH_3(2:5)	116°	,,	,,	,,
o-OCH_3	115°	$C_{13}H_{14}O_3N_2S$	10.0	10.1
p-OCH_3	116°	,,	,,	,,

The author thank Dr. R. D. Desai for his interest in the work and the Ahmedabad Education Society for defraying the expenses incurred during the course of this work.

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OXYFLUOBORATES AND THEIR CHEMICAL ANALOGY WITH SULPHATES PART II. OXYFLUOBORATES OF Cu, Zn, Cd, Co AND Ni

By Asimbikash Ray and Grihapati Mitra

The oxyfluoborates of copper, zinc cobalt, cadmium, and nickel have been prepared. This copper salt crystallises out with five molecules of water; Zn salt with 7, Co salt with 6 and 7, Ni salt with 7 and 6 and the Cd salt with 8/3 molecules of water. All these compounds are highly soluble in water. Some of them are soluble also in 60% alcohol to a great extent. These compounds form mixed crystals with the corresponding sulphates. Some of these compounds are hygroscopic. These compounds decompose at a high temperature with evolution of boron trifluoride. The equivalent conductivities of zinc oxyfluoborate solutions reveal that in solution the compound affords only two ions Zn^{+} and BF_3O^{2-}. The solutions of these compounds give instantaneous precipitation with barium chloride and the precipitates are insoluble in hydrochloric acid.

In Part I of this series (this *issue*, p. 617) the structure of the oxyfluoborate ion has been discussed and in this connection it has been pointed out that the oxyfluoborates should exhibit resemblance with the corresponding sulphates in composition as well as in chemical properties. The oxyfluoborates of the alkali and the alkaline earth metals have been described before; the present paper deals with the methods of preparation and properties of the oxyfluoborates of other metals such as copper, zinc, cadmium, cobalt and nickel.

Other fluoride, oxyfluoride or hydroxyfluoride complex ions, behaving like the sulphate group, have been studied before (Ray, *Z. anorg. allgem. Chem.*, 1932, **206**, 209; 1939, **241**, 165; Lange, *Ber.*, 1927, **60**, 962; 1928, **61**, 799; Mitra, this *Journal*, 1956, **33**, 45). The oxyfluoborates of the metals, mentioned above, differ from the corresponding fluoberyllates and monofluophosphates in being excessively soluble in water, and some of them are also highly soluble in 60% alcohol.

These hydrated salts resemble the corresponding sulphates in their composition as well as in their chemical properties. Even cadmium oxyfluoborate maintains its interesting property of crystallising with 8/3 molecules of water.

Experimental

C. P. quality materials were used for the preparation of these compounds. The standard methods of analysis (Scott, "Standard Methods for Chemical Analysis", D. Van Nostrand Co., New York) were followed for the quantitative analysis of the respective constituents.

Copper Oxyfluoborate Pentahydrate, $CuBF_3O, 5H_2O$.—To copper carbonate (5.5 g.) containing about 57.5% of Cu, taken in a platinum basin and moistened with water, hydrofluoric acid (40%) was added cautiously to decompose all the carbonate. The resulting mass was then warmed on a water-bath for a few minutes in order to decompose the last traces of carbonates About 25 c.c. of water was then added, followed by the addition of 3.1 g. of boric acid. The whole mixture

was digested on the water-bath till the boric acid dissolved. To this mixture 2.5 c.c. of 40% hydrofluoric acid was added according to the equation :

$$CuF_2 + H_3BO_3 + HF = CuBF_3O + 2H_2O.$$

This mixture was digested on a water-bath for about 15 minutes and to it 12*N*-HNO_3 was added dropwise with stirring till almost a clear solution was obtained. To this solution approximately 25 c.c. of water was added, followed by a few drops of hydrofluoric acid. The whole mass was digested on the water-bath for about 1 hour. It was cooled to room temperature (30°), filtered and concentrated in a vacuum desiccator (H_2SO_4). The blue transparent crystals obtained after a few days were filtered under suction, washed quickly with 60% alcohol and dried between the folds of a filter paper. (Found : F, 23.90; Cu, 26.84; B, 4.50. $CuBF_3O$, $5H_2O$ requires F, 24.05; Cu, 26.38; B, 4.56%).

Copper oxyfluoborate is highly soluble in water and hygroscopic. It is also soluble in 60% alcohol. It formed mixed crystals with the corresponding sulphate. The X'ray diffraction study has, however, revealed that they are not isomorphous. (Das Gupta, Ray and Mitra, this *Journal*, 1958, **35**, 185).

Nickel Oxyfluoborate Heptahydrate, $NiBF_3O$, $7H_2O$.—Nickel carbonate (7 g.) containing nearly 42% of nickel, boric acid (3.1 g.) and 40% hydrofluoric acid (2.5 c.c.) were heated exactly in a similar way, as described before for the preparation of this compound. The green crystals obtained were washed with 60% alcohol and dried between the folds of a filter paper. (Found : F, 21.10 ; Ni, 21.82; B, 4.00. $NiBF_3O$, $7H_2O$ requires F, 21.23 ; Ni, 21.86 ; B, 4.03%).

This heptahydrated compound was obtained when the mother-liquor was allowed to concentrate at a low temperature. When the solution was allowed to concentrate on the water-bath, the green crystals were found to contain 23.20% of nickel. It may be suggested in keeping with the observations made before (Ray, *loc. cit.*; Mitra, *loc. cit.*) that this compound is hexahydrated nickel oxyfluoborate. ($NiBF_3O$, $6H_2O$ requires Ni, 23.42%).

Cobalt oxyfluoborate heptahydrate, $CoBF_3O$, $7H_2O$ was obtained as pink-coloured crystals. (Found : F, 21.38 ; Co, 21.78; B, 4.07. $CoBF_3O$, $7H_2O$ requires F, 21.20 ; Co, 21.98 ; B, 4.03%).

It is also highly soluble in water and on heating to 40° becomes blue in colour.

When a solution of heptahydrated cobalt oxyfluoborate was allowed to crystallise on a water-bath, the crystals were found to contain 23.28% of cobalt. Careful heating of the heptahydrated salt in the vicinity of 75° yielded the compound which was found to contain 23.28% of cobalt. These observations suggest that in both the cases the hexahydrated salts are formed. ($CoBF_3O$, $6H_2O$ requires Co, 23.50%).

As the preparation of the oxyfluoborates necessitated the addition of nitric acid, the ferrous oxyfluoborate could not be prepared.

Zinc oxyfluoborate heptahydrate, $ZnBF_3O$, $7H_2O$, was obtained in the same way as the copper compound from zinc carbonate (5.7 g.) containing approximately

57.56% of zinc, boric acid (3.1 g.) and 40% hydrofluoric acid (2.5 c.c.). (Found: F, 20.53; Zn, 23.80; B, 3.92. $ZnBF_3O$, $7H_2O$ requires F, 20.70; Zn, 23.75; B, 3.93%).

These white crystals are slightly hygroscopic and highly soluble in water. $ZnBF_3O$, $7H_2O$ was also prepared without the addition of nitric acid during the procedure; the yield was, however, very poor.

$ZnBF_3O$, $7H_2O$ was dissolved in water and the conductivity of the solutions at different concentrations was measured by the usual method.

TABLE I

Conc. of the soln.	M/32	M/64	M/128	M/256	M/1024
Conductivity	56	78	102	140	158

If it is considered that the equivalent conductivity at infinite dilution increases by about 2% per degree, λ_0 becomes approximately equal to 120 at 18°. At the same temperature $\lambda_0 = 130.1$ for KCl. The compound $ZnBF_3O$ therefore dissociates into two ions in solution according to the equation:

$$ZnBF_3O \rightleftharpoons Zn^{2+} + BF_3O^{2-}$$

Cadmium oxyfluoborate 8/3 *hydrate*, $CdBF_3O$, 8/3 H_2O was prepared as above from cadmium carbonate (8.6 g.), boric acid (3.1 g.) and 40% HF (2.5 c.c.). (Found: F, 23.12; Cd, 45.74; B, 4.47. $CdBF_3O$, 8/3 H_2O requires F, 23.34; Cd, 46.03; B, 4.43%).

This white salt is extremely hygroscopic and easily goes into solution in 60% alcohol.

All these soluble oxyfluoborates could be recrystallised from aqueous solutions. Hence BF_3O^{2-} ion is stable in solution and does not undergo any appreciable dissociation. They gave instantaneous precipitation with barium chloride solution. The white precipitate formed was insoluble in hydrochloric acid. These compounds when heated, started losing water molecules. No other hydrated forms could, however, be isolated in this investigation. At higher temperatures the compounds were found to decompose and BF_3 gas was evolved.

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SHORT NOTES

THE SAPOGENIN FROM SEEDS OF *ACHYRANTHES ASPERA* LINN

By Hari Narayan Khastgir, S. K. Sengupta and P. Sengupta

In a previous communication (Khastgir and Sengupta, this *Journal*, 1958, **35**, 529), we have described the isolation of a triterpene acid, oleanolic acid, from the roots of *Achyranthes aspera* Linn. Gopalachari and Dhar (*J. Sci. Ind. Res.*, 1952, **11B**, 209) isolated a saponin in 2% yield from the defatted seeds of the same shrub, and on acid hydrolysis of the saponin, obtained a sapogenin, m.p. 305-306° (acetate, m.p. 298-300°; 3:5-dinitrobenzoate, m.p. 290-91°) to which they assigned the molecular formula, $C_{29}H_{46}O$.

We have isolated a crude sapogenin fraction from the seeds of *A. aspera* and separated it into three fractions: (*a*) neutral, (*b*) acid, potassium salt of which is sparingly soluble in water and (*c*) acid, potassium salt of which is soluble in water. The neutral fraction (*a*) on repeated chromatography over alumina did not yield any crystalline material. The acid fraction (*b*) yielded oleanolic acid in 1.1% yield, which was characterised through its acetate, methyl ester and methyl ester acetate. The acid fraction (*c*) did not yield any crystalline acid.

Procedure.—The crude sapogenin, obtained in the same manner, as described in our previous communication (*loc. cit.*), from dried and powdered seeds (500 g.) was filtered, dried and extracted in a Soxhlet apparatus with ether for 6 hours. The ether solution was washed with 3% aqueous potassium hydroxide solution, when a flocculent precipitate was obtained. The water layer was filtered after separation from the ether layer.

The ether layer was washed with water until neutral, dried over anhydrous sodium sulphate and evaporated, when 0.85 g. of a gummy neutral material was obtained. On chromatography over activated alumina (50 g.), almost the entire material (0.81 g.) was eluted with petroleum ether (b.p. 60-80°) as a gum, from which no crystalline solid could be isolated even after repeated chromatography.

The aqueous alkaline solution, after the separation of the sparingly soluble potassium salt, was acidified and extracted with ether. The ether solution was washed with water, dried over anhydrous sodium sulphate and evaporated, when 0.52 g. of a dark tarry mass was obtained, which resisted all attempts at crystallisation.

The sparingly soluble potassium salt was acidified with cold and dilute HCl and extracted with ether. The ether solution was washed with water, dried over anhydrous sodium sulphate and evaporated, when 6.1 g. of a crystalline acid, m.p. 292-300°, was obtained.

Oleanolic Acid.—The above acid on crystallisation from a mixture of chloroform and methanol gave colorless crystals of oleanolic acid, m.p. 303-305°, $[\alpha]_D^{31}$ + 79° ($CHCl_3$), (5.6 g., 1.1% on the basis of dried seeds).

Oleanolic Acid Acetate.—The acetate was prepared in the usual manner with acetic anhydride and pyridine. On crystallisation from acetone, it melted at 262-65°, $[\alpha]_D^{31}$ + 77.5° ($CHCl_3$). The mixed m.p. of the acetate with an authentic specimen of oleanolic acid acetate did not show any depression.

Methyl Oleanolate.—The acid on treatment with an ethereal solution of diazomethane gave methyl oleanolate, which after crystallisation from acetone gave colorless crystals, m.p. 197-98°, $[\alpha]_D^{30}$ + 77° ($CHCl_3$).

Methyl Oleanolate Acetate.—The above ester on acetylation with acetic anhydride and pyridine gave methyl oleanolate acetate, which after crystallisation from acetone gave colorless crystals, m.p. 215-16°, $[\alpha]_D^{31}$ + 71° ($CHCl_3$). The mixed m.p. with an authentic specimen of methyl oleanolate acetate did not show any depression. (Found : C, 77.71 ; H, 10.00. Calc. for $C_{33}H_{52}O_4$: C, 77.29 ; H, 10.22%).

Sincere thanks of the authors are due to Mr. Priyalal Moulik for the optical rotation study of the compounds and to Mr. N.C. Guha, Research Director, E.I.P.W. Ltd., Calcutta for his encouragement.

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dl-SERINE

By S. K. Guha and J. N. Ray

Mahajani and Ray (this *Journal*, 1956, **33**, 455) described an intermediate compound, m.p. 62-64°, in their synthesis of serine. We now find that this substance is hydrated sodium acetate mixed with organic material from which no serine can be isolated. Therefore, the whole synthesis has been repeated. We describe below the revised process.

Methyleneaminoacetonitrile (3.4 g.) was suspended in alcohol (50 c.c.) and warmed to 50°, and in another flask paraformaldehyde (3 g.) was dissolved in absolute alcohol (25 c.c.) by warming (addition of two drops of sodium ethoxide solution described below helps dissolution). The paraformaldehyde solution was gradually added to the suspension of methyleneaminoacetonitrile in alcohol, taking care that temperature did not rise above 55°. A solution of sodium ethoxide (Na, 1.15 g. and alcohol, 25 c.c.) was added to the above mixture with shaking, temperature being kept at 54°. In an hour a clear solution resulted and the solution was maintained at 54° for 2 hours. The solution was then kept at 50° for 12 hours. It acquired a yellowish tinge and some sodium formate separated.

The solution was then concentrated *in vacuo* to about 30 c.c. when a slight evolution of ammonia was noticed. It was then mixed with 33 c.c. of 5% alcoholic KOH (95% alcohol was used) and refluxed on the steam-bath. After 2 hours, the mixture was left overnight at the room temperature. Next morning, solids [CH_2=N.CH.(CH_2OH).COOK], were collected and washed with alcohol. The filtrate obtained at this stage was treated as under (B) below. The solids (1.5 to 1.8 g.) were dissolved in water (10 c.c.) and to the solution was added 10% H_2SO_4 (10 c.c.). The mixture was then heated to 90° for 2 hours when formaldehyde was evolved and the CH_2=N group was completely hydrolysed. A part of the solution was neutralised with alkali and then made just acidic with HCl. The solution was spotted on Whatman filter paper No. 1, along with authentic samples of serine and glycine and run for 6 hours with the Patridge solvent (butanol-acetic acid-water). After drying in air the paper was sprayed with ninhydrin solution. The spot exactly corresponded to serine. R_f in HCl=0.31 (serine and the substance), R_f=0.24 in the case of both in H_2SO_4. From the above, the structure of potassium salt was inferred.

From the bulk of the hydrolysed solution, serine can be isolated by any of the usual methods. After the removal of excess of H_2SO_4 with lead carbonate, filtration, and removal of lead with H_2S, the solution on concentration *in vacuo* gives serine, m.p. and mixed m.p. 246° (decomp.), yield 1.3 g.

Filtrate B: It was slowly evaporated on the water-bath and the residue was separately hydrolysed with 10% H_2SO_4. The hydrolysed solution on chromatogram gave four spots, of which two were that of glycine and serine and the other two, we presume, were that of methyleneserine and methyleneglycine.

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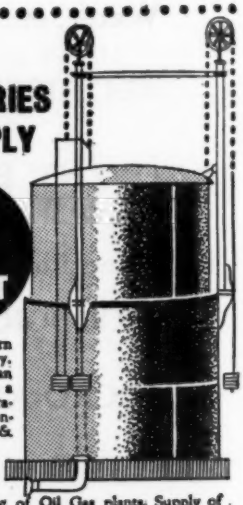

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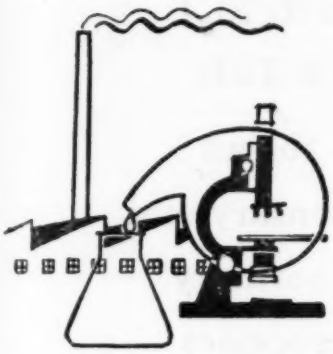

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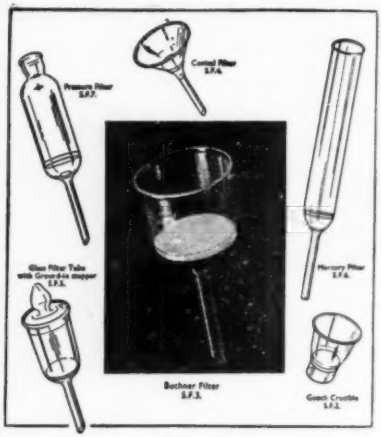

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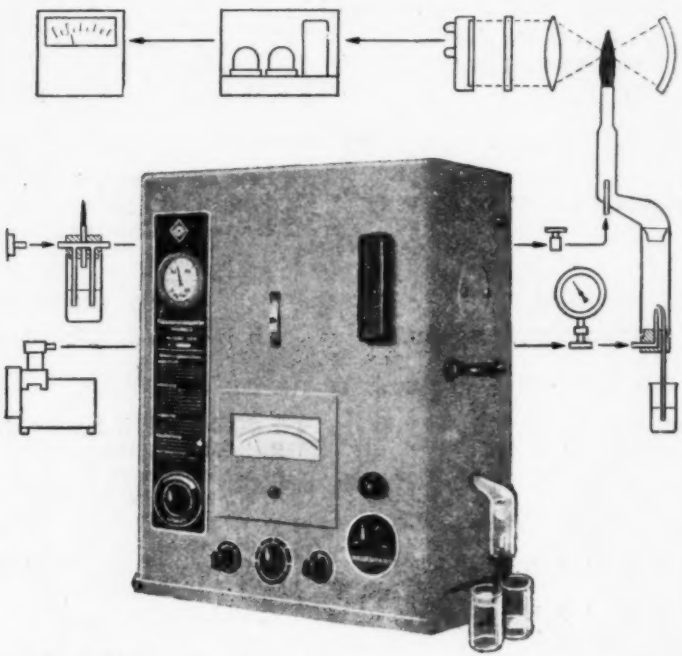

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